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**INVESTIGATION OF THE MICROWAVE  
PROPERTIES OF FERROELECTRICS**

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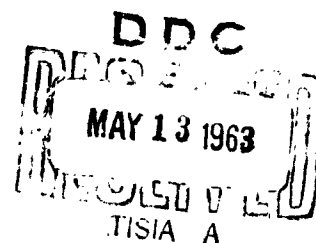
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**FINAL REPORT**  
**AF 19 (604)-8005**

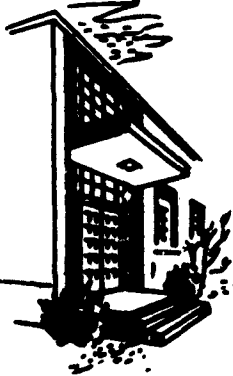
B.D. Silverman  
R. I. Joseph  
W.M. Winter

20 January 1961 - 19 January 1963

Project 4600  
Task 460003



Research Division  
Raytheon Company  
Waltham 54, Massachusetts



Prepared for  
**ELECTRONICS RESEARCH DIRECTORATE**  
**AIR FORCE CAMBRIDGE RESEARCH LABORATORIES**  
**OFFICE OF AEROSPACE RESEARCH**  
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## ABSTRACT

A systematic and fundamental study has been made of the microwave properties of ferroelectric materials with the perovskite structure. The quantities singled out for investigation are nonlinear dielectric constant, microwave losses and electrostriction. The comparison between theory and experiment is discussed.

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## 1. INTRODUCTION

A systematic and fundamental study has been made of the microwave properties of ferroelectric materials with the perovskite structure. These materials have been chosen due to their microwave device potential.<sup>1</sup> The quantities singled out for investigation were nonlinear dielectric constant, microwave losses and electrostriction. Single crystalline studies were performed mainly on strontium titanate due to the relatively good samples available.<sup>2</sup>

Due to recent ideas<sup>3</sup> concerning the dynamical aspects of ferroelectricity it has been possible to gain some insight into the origin of the observed microwave loss of materials in the unpolarized phase.<sup>4</sup> One component of microwave loss appears to result from the presence of imperfections in the crystal. Better sample preparation should be able to minimize this contribution to the loss. There also appears to be a contribution to the loss which arises from anharmonic interactions in the lattice. Since anharmonic interactions also contribute to the nonlinearities, low loss contribution from the anharmonic terms might seem to imply low nonlinearity. However, since the anharmonic loss depends on the details of the frequency spectrum and the nonlinearity depends on only the properties of long waves, low anharmonic loss and large anharmonic nonlinearity are, strictly speaking, not mutually exclusive.

---

<sup>1</sup>"Study of Nonlinear Microwave Ferroelectric Devices," Contract No. AF 33(616)-8022, WADD, Interim Engineering Report No. 1 (1 March 1961 - 31 May 1961).

<sup>2</sup>Samples were obtained from National Lead.

<sup>3</sup>W. Cochran, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis Ltd., London, 1960), Vol. 9, p. 387; P. W. Anderson, paper given at All-Union Conference on Dielectrics, Moscow, 1958 (Bull. Acad. Sci. USSR, 1960), Vol. 24; R. Landauer, H. Juretschke, and P. Sorokin (unpublished manuscript).

<sup>4</sup>B. D. Silverman, *Phys. Rev.* 125, 1921 (1962).

In section 2 of this report a procedure is developed to systematically interpret the origin of the various contributions to the dielectric constant. Not only are anharmonic terms in the lattice potential energy considered, but also electron deformation terms.<sup>5</sup> One usually fits the temperature dependence of the dielectric constant with an expression of the following form:

$$\epsilon = \frac{C}{T - T_c} + \text{const.}$$

In section 2 it is shown that the constant cannot be interpreted as arising solely from the presence of electronic polarizability and other hard modes of the lattice; electron deformation terms also contribute to this constant. It is interesting to speculate that large electronic deformations (large second order moment) should contribute to a large third order potential (as Szigeti has shown). Since the third order potential is responsible for the broadening of the "ferroelectric" absorption line, the broad lines that are observed could result from large electronic deformation. It seems reasonable that there should be relatively large electronic deformation associated with the large amplitude of the soft mode. Of course large amplitude also leads to large lattice anharmonicities.

In section 3 the calculation of the dielectric constant has been extended to include nonlinear effects. Large nonlinearity is essential for the eventual use of ferroelectric materials in many microwave applications.

The nonlinear response is different for crystals which are clamped or unclamped with respect to the probing field. A measure of this difference is obtained from the electrostrictive constants of the material. While there have been many measurements of the electrostrictive and piezoelectric coefficients, there has been no theory relating the results of measurements to the microscopic parameters of the lattice. In section 4 such a theory has been developed. It is believed that results of this calculation will assist in enhancing our understanding of the requirements of useful materials.

---

<sup>5</sup>B. Szigeti, Proc. Roy. Soc. (London) A252, 217 (1959).

## **2. TEMPERATURE DEPENDENCE OF THE DIELECTRIC CONSTANT OF FERROELECTRIC MATERIALS**

### **2.1 Introduction**

Above the ferroelectric transition, the dielectric constant of  $\text{BaTiO}_3$  and related isomorphs is large and exhibits a Curie-Weiss type temperature dependence. It has been suggested that this behavior results from a near cancellation of the short range restoring forces and the long range driving forces on the ions.<sup>1</sup> Anharmonic terms in the lattice potential energy are held responsible for the temperature dependence of the dielectric constant. Since the Curie temperature is positive, the anharmonic interactions stabilize the system above its transition temperature. Cochran<sup>2</sup> has suggested that the Curie-Weiss behavior of the dielectric constant results from the temperature dependence of a long wave length transverse optical mode of the lattice. The suggested temperature dependence of this mode has been observed by Barker and Tinkham.<sup>3</sup> At the transition temperature the frequency of this mode should go to zero and the lattice displacements associated with this mode become unstable. A transition is made to the ferroelectric state. If the anharmonic interactions do stabilize the system above the transition temperature, the harmonic part of the frequency associated with this mode is an imaginary quantity. One cannot systematically consider the effects of anharmonic interactions on the equilibrium properties of a ferroelectric in the unpolarized phase by expanding the free energy in powers of the anharmonic coupling coefficients about the harmonic state. Such an expansion would lead to divergences. To avoid this difficulty, all quantities should be expanded about their thermal averages.<sup>4</sup> In this manner one can systematically derive the thermal equilibrium properties of a ferroelectric in its unpolarized phase.

In this paper we will derive an expression for the temperature dependent dielectric constant in the unpolarized phase of a ferroelectric which manifests a vibrational instability at a positive temperature.<sup>5</sup> We will consider a Hamiltonian such as Szigeti<sup>6</sup> treated in discussing the

temperature dependence of the dielectric constant of the alkali halides. Therefore, not only will third and fourth order anharmonic terms in the potential energy expansion be considered, but also electron cloud deformation through the presence of a second and third order electronic moment. It will be shown that the exact linear response can be obtained for this Hamiltonian. The fourth order anharmonic interaction with a positive coupling coefficient stabilizes the system. Third order anharmonic interactions of either sign raise the instability temperature. The largest effect due to the presence of the electronic deformation terms is the contribution of a constant term to the dielectric constant at temperatures high compared with the Curie temperature. This indicates that one cannot unambiguously assign the origin of such a term to the other "hard" optical modes of the lattice.

## 2.2 Temperature Dependent Dielectric Constant

The Hamiltonian of the system is

$$\begin{aligned}
 H = & \sum_k \hbar \omega_k^a (a_k^{a*} a_k^a + \frac{1}{2}) + \sum_k \hbar \omega_k^o (a_k^{o*} a_k^o + \frac{1}{2}) + \frac{1}{2} (p_o^2 - \omega_o^2 q_o^2) \\
 & - \alpha E \sqrt{N} q_o^o + \sum_k \left\{ \frac{q_o^o}{\sqrt{N}} F(k) + EA(k) \right\} \frac{\hbar}{\sqrt{\omega_k^o \omega_k^a}} (a_k^a + a_{-k}^{a*}) (a_{-k}^o + a_k^{o*}) \\
 & + \sum_k \left\{ \frac{q_o^2}{N} G^o(k) + E \frac{q_o^o}{\sqrt{N}} B^o(k) \right\} \frac{\hbar}{\omega_k^o} (a_k^o + a_{-k}^{o*}) (a_{-k}^o + a_k^{o*}) \\
 & + \sum_k \left\{ \frac{q_o^2}{N} G^a(k) + E \frac{q_o^o}{\sqrt{N}} B^a(k) \right\} \frac{\hbar}{\omega_k^a} (a_k^a + a_{-k}^{a*}) (a_{-k}^a + a_k^{a*}) \\
 = & H_1 + H_2 + \frac{1}{2} (p_o^2 - \omega_o^2 q_o^2) - \alpha E \sqrt{N} q_o^o + H_3 + H_4 + H_5 .
 \end{aligned} \tag{1}$$

The only difference between this Hamiltonian and the one treated by Szigeti<sup>6</sup> appears in the third term. All long wavelength transverse optical modes which are unstable in the harmonic approximation have been collectively labelled with zero wave vector and assigned an imaginary frequency.<sup>7</sup> This procedure is possible since the total number of such wavelengths is small compared with the total number of wavelengths of the optical branch.<sup>8</sup>  $q_0^o$  and  $p_0^o$  are the normal mode coordinate and conjugate momentum respectively of this long wavelength transverse mode. The sums over  $k$  do not include this mode. The  $a_k^{o*}$  and  $a_k^o$  are just the usual creation-destruction operators for an optical mode of wave vector  $k$  which satisfy the following commutation relations

$$[a_k, a_{k'}] = [a_k^*, a_{k'}^*] = 0 ; [a_k, a_{k'}^*] = \delta_{kk'} .$$

Superscript  $a$  refers to an acoustic mode.  $N$  is the number of ion pairs. The calculation is performed for two atoms per unit cell and the optical mode of this model is chosen as the soft temperature dependent ferroelectric mode. This enables us to calculate the temperature dependence of the dielectric constant resulting from the soft mode. Contributions to the dielectric constant arising from other optical vibrations appear just as additive constants in the final result. The  $\alpha$ ,  $A(k)$  and  $B(k)$  describe the linear, second, and third order moments respectively. The  $F(k)$  and  $G(k)$  describe the third and fourth order anharmonic couplings respectively.  $E$  is the macroscopic field. The  $\omega_k^a$  and  $\omega_k^o$  are the frequencies of the acoustical and optical mode having wave vector  $k$ . The negative of  $\omega_0^{o2}$  is the square of the imaginary harmonic frequency of the unstable transverse optical long wavelength mode. This Hamiltonian has been derived by the assumption of a cubic structure with a center of symmetry for the material under consideration. The ideal perovskite structure fulfills these requirements.

The Hamiltonian [Eq. (1)] is transformed by a unitary transformation

$$e^{-iS} H e^{iS} = H + i[H, S] - \frac{1}{2} [[H, S], S] + \dots \quad (2)$$

with transformation operator  $S$  given by

$$S = i \frac{q_0^0}{\sqrt{N}} \sum_k \omega_k^0 g(k) (a_k^a + a_{-k}^{a*}) (a_{-k}^o - a_k^{o*}) \\ - i \frac{q_0^0}{\sqrt{N}} \sum_k \omega_k^a g(k) (a_k^a - a_{-k}^{a*}) (a_{-k}^o + a_k^{o*}) \quad (3)$$

This form has been chosen for  $S$  so that  $H_3$  can be eliminated from the transformed Hamiltonian by suitably choosing the  $g(k)$ .

$$i[(H_1 + H_2), S] + H_3 = 0 \quad (4)$$

Therefore

$$g(k) = \frac{\sqrt{N}}{q_0^0} \left\{ \frac{q_0^0}{\sqrt{N}} F(k) + EA(k) \right\} \frac{1}{\sqrt{\omega_k^o \omega_k^a}} \frac{1}{(\omega_k^a - \omega_k^o)} \quad (5)$$

since

$$[(H_1 + H_2), S] = -\frac{i q_0^0 \pi}{\sqrt{N}} \sum_k g(k) (\omega_k^{o2} - \omega_k^{a2}) (a_k^a + a_{-k}^{a*}) (a_{-k}^o + a_k^{o*}) \quad (6)$$



Other commutation relations of use are:

$$[H_3, S] = 2i \sum_k \left| \frac{q_0^0}{\sqrt{N}} F(k) + EA(k) \right|^2 \frac{\pi}{\omega_k^0 (\omega_k^a - \omega_k^0)^2} (a_k^0 + a_{-k}^{0*}) (a_{-k}^0 + a_k^{0*}) \quad (7)$$

$$-2i \sum_k \left| \frac{q_0^0}{\sqrt{N}} F(k) + EA(k) \right|^2 \frac{\pi}{\omega_k^a (\omega_k^a - \omega_k^0)^2} (a_k^a + a_{-k}^{a*}) (a_{-k}^a + a_k^{a*})$$

$$[H_4, S] = -4i \sum_k \left\{ \frac{q_0^0}{N} G^0(k) + E \frac{q_0^0}{\sqrt{N}} B^0(k) \right\} \frac{q_0^0}{\sqrt{N}} \pi g(k) (a_{-k}^0 + a_k^{0*}) (a_k^a + a_{-k}^{a*}) \quad (8)$$

$$[H_5, S] = 4i \sum_k \left\{ \frac{q_0^0}{N} G^a(k) + E \frac{q_0^0}{\sqrt{N}} B^a(k) \right\} \frac{q_0^0}{\sqrt{N}} \pi g(k) (a_k^a + a_{-k}^{a*}) (a_{-k}^0 + a_k^{0*}) \quad (9)$$

$$\begin{aligned} \left[ (H_1 + H_2), S \right] &= 2 \sum_k \left| \frac{q_0^0}{\sqrt{N}} F(k) + EA(k) \right|^2 \frac{\pi}{\omega_k^0 (\omega_k^0 - \omega_k^a)^2} (a_k^0 + a_{-k}^{0*}) (a_{-k}^0 + a_k^{0*}) \\ &\quad - 2 \sum_k \left| \frac{q_0^0}{\sqrt{N}} F(k) + EA(k) \right|^2 \frac{\pi}{\omega_k^a (\omega_k^0 - \omega_k^a)^2} (a_k^a + a_{-k}^{a*}) (a_{-k}^a + a_k^{a*}) \end{aligned} \quad (10)$$

The following relations have been used to write the preceding results in the form shown:

$$G^a(-k) = G^a(k), \quad B^a(-k) = B^a(k)$$

With the use of these commutation relations, the transformed Hamiltonian  $H_T$  can be written

$$\begin{aligned}
H_T = & \sum_k \hbar \omega_k^a (a_k^a a_k^{a*} + \frac{1}{2}) + \sum_k \hbar \omega_k^o (a_k^o a_k^{o*} + \frac{1}{2}) + \frac{1}{2} (p_o^2 - \omega_o^2 q_o^2) - \alpha E \sqrt{N} q_o^o \\
& + \sum_k \left\{ \frac{q_o^2}{N} G^o(k) + E \frac{q_o^o}{\sqrt{N}} B^a(k) \right\} \frac{\pi}{\omega_k^o} (a_k^o + a_{-k}^{o*}) (a_{-k}^o + a_k^{o*}); \\
& + \sum_k \left\{ \frac{q_o^2}{N} G^a(k) + E \frac{q_o^o}{\sqrt{N}} B^o(k) \right\} \frac{\pi}{\omega_k^a} (a_k^a + a_{-k}^{a*}) (a_{-k}^a + a_k^{a*}) \\
& - \sum_k \left| \frac{q_o^o}{\sqrt{N}} F(k) + EA(k) \right|^2 \frac{\pi}{\omega_k^o (\omega_k^a - \omega_k^o)} (a_k^o + a_{-k}^{o*}) (a_{-k}^o + a_k^{o*}) \\
& + \sum_k \left| \frac{q_o^o}{\sqrt{N}} F(k) + EA(k) \right|^2 \frac{\pi}{\omega_k^a (\omega_k^a - \omega_k^o)} (a_k^a + a_{-k}^{a*}) (a_{-k}^a + a_k^{a*}) \\
& + 4 \sum_k \left\{ \frac{q_o^2}{N} G^o(k) + E \frac{q_o^o}{\sqrt{N}} B^o(k) \right\} \left\{ \frac{q_o^o}{\sqrt{N}} F(k) + EA(k) \right\} \frac{\pi}{(\omega_k^o \omega_k^a)^{1/2} (\omega_k^a - \omega_k^o)} (a_{-k}^o + a_k^{o*}) (a_k^a + a_{-k}^{a*}) \\
& - 4 \sum_k \left\{ \frac{q_o^2}{N} G^a(k) + E \frac{q_o^o}{\sqrt{N}} B^a(k) \right\} \left\{ \frac{q_o^o}{\sqrt{N}} F(k) + EA(k) \right\} \frac{\pi}{(\omega_k^o \omega_k^a)^{1/2} (\omega_k^a - \omega_k^o)} (a_{-k}^o + a_k^{o*}) (a_k^a + a_{-k}^{a*}) \\
& - \frac{1}{2} [H'', S], S] + \dots
\end{aligned} \tag{11}$$

where  $H''$  is  $H - (H_1 + H_2)$ .

Terms linear in the third order anharmonic coupling coefficient  $F(k)$  and second order moment coefficient  $A(k)$  have been eliminated from the Hamiltonian. Terms bilinear in both coefficients do, however, appear. The preceding transformation has been performed since only the terms diagonal in the creation-destruction operator that we have exhibited explicitly in the Hamiltonian [Eq. (11)] will contribute to the linear response of the system. This will be shown in what follows. Let us group the diagonal terms and label them  $H_D$ . Since the state of thermal equilibrium will be considered, one can also set

$$a_k^* a_k = a_{-k}^* a_{-k} \quad (12)$$

Therefore

$$\begin{aligned} H_D = & \sum_k \hbar \omega_k^a (a_k^{a*} a_k^a + \frac{1}{2}) + \sum_k \hbar \omega_k^o (a_k^{o*} a_k^o + \frac{1}{2}) \\ & + \frac{1}{2} \{ p_o^2 + [ \frac{4}{N} \sum_k \frac{\hbar}{\omega_k^o} G^o(k) (a_k^{o*} a_k^o + \frac{1}{2}) + \frac{4}{N} \sum_k \frac{\hbar}{\omega_k^a} G^a(k) (a_k^{a*} a_k^a + \frac{1}{2}) ] \\ & - \frac{4}{N} \sum_k |F(k)|^2 \frac{\hbar}{\omega_k^o (\omega_k^{a2} - \omega_k^{o2})} (a_k^{o*} a_k^o + \frac{1}{2}) \\ & + \frac{4}{N} \sum_k |F(k)|^2 \frac{\hbar}{\omega_k^a (\omega_k^{a2} - \omega_k^{o2})} (a_k^{a*} a_k^a + \frac{1}{2}) - \omega_o^2 \} q_o^2 \end{aligned} \quad (13)$$

$$\begin{aligned}
& - \alpha E \sqrt{N} q_0^0 + \frac{2E q_0^0}{\sqrt{N}} \sum_k B^0(k) \frac{\pi}{\omega_k^0} (a_k^{0*} a_k^0 + \frac{1}{2}) + \frac{2E q_0^0}{\sqrt{N}} \sum_k B^a(k) \frac{\pi}{\omega_k^a} (a_k^{a*} a_k^a + \frac{1}{2}) \\
& - \frac{4E q_0^0}{\sqrt{N}} \sum_k F(k) A(-k) \frac{\pi}{\omega_k^0 (\omega_k^a - \omega_k^0)} (a_k^{0*} a_k^0 + \frac{1}{2}) + \frac{4E q_0^0}{\sqrt{N}} \sum_k F(k) A(-k) \frac{\pi}{\omega_k^a (\omega_k^a - \omega_k^0)} (a_k^{a*} a_k^a + \frac{1}{2}) \\
& - 2E^2 \sum_k |A(k)|^2 \frac{\pi}{\omega_k^0 (\omega_k^a - \omega_k^0)} (a_k^{0*} a_k^0 + \frac{1}{2}) + 2E^2 \sum_k |A(k)|^2 \frac{\pi}{\omega_k^a (\omega_k^a - \omega_k^0)} (a_k^{a*} a_k^a + \frac{1}{2}) .
\end{aligned}$$

The partition function of the system is

$$Z = \sum_n \langle n | e^{-\beta H_T} | n \rangle = \sum_n \langle n | e^{-\beta H_D - \beta H'} | n \rangle ; \beta = \frac{1}{RT} . \quad (14)$$

$H'$  contains all terms nondiagonal in the creation-destruction operator and diagonal terms originating from  $[H', S], S$  and higher order commutators.

Expand the partition sum in powers of  $H'$

$$Z = \sum_n \langle n | e^{-\beta H_D} | n \rangle + \sum_n \sum_{n'=1}^{\infty} (-1)^{n'} \int_0^{\beta} d\lambda_1 \int_0^{\lambda_1} d\lambda_2 \int_0^{\lambda_2} d\lambda_3 \dots \int_0^{\lambda_{n'-1}} d\lambda_{n'} \langle n | e^{\lambda_1 H_D} H' e^{(\lambda_2 - \lambda_1) H_D} H' \dots$$

(15)

$$e^{-\lambda_{n'} H_D} | n \rangle = Z^0 + Z' .$$

It will be shown that in the limit of infinite normalization volume, i.e.  $N \rightarrow \infty$ ,  $Z'$  will not contribute to the linear response. The free energy  $F$  can be written

$$F = -\frac{1}{\beta} \ln Z \quad (16)$$

and hence the polarization is given by

$$P = -\frac{\partial F}{\partial E} = \frac{1}{\beta Z} \frac{\partial Z}{\partial E} \quad (17)$$

To obtain the linear response it is therefore only necessary to examine at most, terms quadratic in the electric field.

Let us consider

$$Z^0 = \sum_n \langle n | e^{-\beta H_D} | n \rangle \quad (18)$$

The trace is evaluated in a representation for which the  $a_k^* a_k$  are diagonal. One can then write

$$Z^0 = \sum_{n_o, n_k} \langle n_o | e^{-\beta H_D(n_k, q_o^0)} | n_o \rangle \quad (19)$$

with  $H_D(n_k, q_o^0)$  given by equation (13), however with  $a_k^* a_k$  and  $a_k^o a_k^o$  replaced by  $n_k^a$  and  $n_k^o$  respectively.  $n_k^a$  and  $n_k^o$  are just the phonon occupation numbers for the  $k^{\text{th}}$  acoustic and optical mode respectively. Note that one can consider the coefficient in front of  $q_o^2$  as the square of an effective frequency  $\Omega$  which is dependent upon the occupation of all nonzero wave vector phonon states.

$$\Omega^2(n_k) = \frac{4}{N} \sum_k \frac{\hbar}{\omega_k} G^o(k) (n_k^o + \frac{1}{2}) + \frac{4}{N} \sum_k \frac{\hbar}{\omega_k} G^a(k) (n_k^a + \frac{1}{2}) \quad (20)$$

$$- \frac{4}{N} \sum_k |F(k)|^2 \frac{\pi}{\omega_k^o(\omega_k^a - \omega_k^o)} (n_k^o + \frac{1}{2}) + \frac{4}{N} \sum_k |F(k)|^2 \frac{\pi}{\omega_k^a(\omega_k^a - \omega_k^o)} (n_k^a + \frac{1}{2}) - \omega_o^2.$$

It will be shown that  $n_k^a$  and  $n_k^o$  can be rigorously replaced by average values  $\bar{n}_k^a$  and  $\bar{n}_k^o$  to be defined. If  $\Omega^2(\bar{n}_k)$  is positive at all temperatures, the material will not make a transition to a ferroelectric state at any temperature. If this quantity changes sign at a temperature for which the phonon occupation numbers can be replaced by their classical values, then

$$\Omega^2 \sim (T - T_C) \quad (21)$$

and above the transition the dielectric constant should follow a Curie-Weiss law. This is observed for such materials as BaTiO<sub>3</sub>, PbTiO<sub>3</sub>, and KNbO<sub>3</sub>. If the square of this frequency changes sign at a temperature for which the phonon occupation numbers deviate significantly from the classical values, then deviations from a Curie-Weiss behavior of the dielectric constant will be observed before the material goes through a phase transformation.<sup>9</sup> This is apparently observed in KTaO<sub>3</sub>.<sup>10</sup>

Since we are interested in the linear response, the partition function is expanded to terms in  $E^2$ . Terms linear in  $E$  are dropped since they will vanish when the average over the  $q_o^o$  coordinate is performed.

$$\begin{aligned}
Z^0 = \sum_{n_0, n_k} \langle n_0 | e^{-\beta \sum_k \hbar \omega_k^a (n_k^a + \frac{1}{2}) - \beta \sum_k \hbar \omega_k^o (n_k^o + \frac{1}{2}) - \frac{\beta}{2} (p_0^2 + \hbar^2 (n_k^o)^2)} \{ 1 + \frac{1}{2} \beta^2 E^2 q_0^2 [ -a \sqrt{N} \\
+ \frac{2}{\sqrt{N}} \sum_k B^o(k) \frac{\pi}{\omega_k^o} (n_k^o + \frac{1}{2}) + \frac{2}{\sqrt{N}} \sum_k B^a(k) \frac{\pi}{\omega_k^a} (n_k^a + \frac{1}{2}) - \frac{4}{\sqrt{N}} \sum_k F(k) A(k) \frac{\pi}{\omega_k^o (\omega_k^a - \omega_k^o)} (n_k^o + \frac{1}{2}) \\
+ \frac{4}{\sqrt{N}} \sum_k F(k) A(-k) \frac{\pi}{\omega_k^a (\omega_k^a - \omega_k^o)} (n_k^a + \frac{1}{2}) ]^2 \\
+ 2\beta E^2 \sum_k |A(k)|^2 \frac{\pi}{\omega_k^o (\omega_k^a - \omega_k^o)} (n_k^o + \frac{1}{2}) \\
- 2\beta E^2 \sum_k |A(k)|^2 \frac{\pi}{\omega_k^a (\omega_k^a - \omega_k^o)} (n_k^a + \frac{1}{2}) \} |n_0 \rangle .
\end{aligned} \tag{22}$$

In the limit of infinite normalization volume i.e.  $N \rightarrow \infty$ , the result of performing the sums over the  $n_k$  is to just replace the  $n_k$  by their thermal average  $\overline{n_k}$  in all terms except the first two appearing in the exponential.  $\overline{n_k}$  is given by

$$\overline{n_k} = \frac{\sum_{n_k} n_k e^{-\beta \hbar \omega_k (n_k + \frac{1}{2})}}{\sum_{n_k} e^{-\beta \hbar \omega_k (n_k + \frac{1}{2})}} . \tag{23}$$

This statement can be proved as follows. Expand all terms in the partition sum about the thermal average  $\bar{n}_k$ , except the first two appearing in the exponential. The first term in the expansion is just equation (22), however with bars appearing over all the  $n_k$  except the first  $n_k^a$  and  $n_k^o$  in the exponential, i.e.

$$Z_o = \sum_{n_o, n_k} \langle n_o | e^{-\beta \sum_k \hbar \omega_k^a (n_k^a + \frac{1}{2}) - \beta \sum_k \hbar \omega_k^o (n_k^o + \frac{1}{2})} R(\bar{n}_k^a, \bar{n}_k^o, q_o^o) | n_o \rangle \quad (24)$$

$R$  is easily defined by comparison of equation (24) with (22). It can be seen that all terms quadratic in the applied field are proportional to the number of ion pairs in the normalization volume. In view of equation (17) the polarization is therefore proportional to the normalization volume as expected.<sup>11</sup>

The next term in the expansion is

$$\sum_{n_o, n_k} \langle n_o | e^{-\beta \sum_k \hbar \omega_k^a (n_k^a + \frac{1}{2}) - \beta \sum_k \hbar \omega_k^o (n_k^o + \frac{1}{2})} \sum_{k'} \frac{\partial R(\bar{n}_k^a, \bar{n}_k^o, q_o^o)}{\partial n_{k'}} \bigg|_{\bar{n}_{k'}} (n_{k'} - \bar{n}_{k'}) | n_o \rangle \quad (25)$$

All such terms vanish identically with use of equation (23). The only nonvanishing term in next order is

$$\sum_{n_o, n_k} \langle n_o | e^{-\beta \sum_k \hbar \omega_k^a (n_k^a + \frac{1}{2}) - \beta \sum_k \hbar \omega_k^o (n_k^o + \frac{1}{2})} \sum_{k'} \frac{1}{2!} \frac{\partial^2 R(\bar{n}_k^a, \bar{n}_k^o, q_o^o)}{\partial n_{k'}^2} (n_k - \bar{n}_{k'})^2 | n_o \rangle \quad (26)$$

Contributions from this term that are quadratic in the applied field vary as  $N^0$  and are therefore neglected. Contributions to the terms independent of the applied field vanish as  $N^{-1}$  when  $N \rightarrow \infty$ . In a similar fashion, it



can be seen that all higher order terms in such an expansion also vanish in the limit of infinite normalization volume. Therefore, fluctuations about the thermal values  $\overline{n_k}$  do not contribute to the linear response.

Similarly one can show that contributions to the linear response from  $H'$  [Eq. (14)] also vanish in the limit of infinite normalization volume. For that part of  $H'$  which is nondiagonal in the creation-destruction operators, there are no linear terms of the form

$$-\sum_n \int_0^\beta d\lambda_1 \langle n | e^{(\lambda_1 - \beta)H_D} H' e^{-\lambda_1 H_D} | n \rangle . \quad (27)$$

The first nonvanishing contribution will come from a term of second order in  $H'$ , namely

$$\sum_n \int_0^\beta d\lambda_1 \int_0^{\lambda_1} d\lambda_2 \langle n | e^{(\lambda_1 - \beta)H_D} H' e^{(\lambda_2 - \lambda_1)H_D} H' e^{-\lambda_2 H_D} | n \rangle . \quad (28)$$

Contributions from this term that are quadratic in the applied field vary as  $N^0$  and are therefore neglected. Contributions to terms independent of the applied vanish as  $N^{-1}$  as  $N \rightarrow \infty$ . In a similar fashion, it can be seen that all higher order terms in such an expansion do not contribute to the linear response. An examination of the terms of  $H'$  that are diagonal in the creation-destruction operators will also show that they cannot contribute to the linear response of the system, so we can write [using Eq. (17) and (24)]

$$P = \frac{1}{\beta Z^0} \frac{\partial Z^0}{\partial E} . \quad (29)$$

Equation (29) is an exact expression for the linear response of the system described by the Hamiltonian given by equation (1) in the limit of infinite normalization volume.

To evaluate  $\overline{Z^0}$ , matrix elements between the zero wave vector states must be taken and then the sums performed over all phonon occupation numbers. Since the final result is independent of the number of  $k = 0$  phonons, this procedure can be simplified by treating  $p_0^0$  and  $q_0^0$  as classical variables. One can therefore write

$$\overline{Z^0} = \int_{-\infty}^{\infty} dp_0^0 \int_{-\infty}^{\infty} dq_0^0 R(\overline{n}_k^a, \overline{n}_k^o, q_0^0) \sum_{n_k} e^{-\beta \sum_k \hbar \omega_k^a (n_k^a + \frac{1}{2}) - \beta \sum_k \hbar \omega_k^o (n_k^o + \frac{1}{2})} \quad (30)$$

which gives

$$\begin{aligned} \overline{Z^0} = & \sum_{n_k} e^{-\beta \sum_k \hbar \omega_k^a (n_k^a + \frac{1}{2}) - \beta \sum_k \hbar \omega_k^o (n_k^o + \frac{1}{2})} \frac{2\pi}{\beta \Omega} \{ 1 + 2\beta E^2 \sum_k |A(k)|^2 \frac{\pi}{\omega_k^o (\omega_k^a{}^2 - \omega_k^o{}^2)} (\overline{n}_k^o + \frac{1}{2}) \\ & - 2\beta E^2 \sum_k |A(k)|^2 \frac{\pi}{\omega_k^a (\omega_k^a{}^2 - \omega_k^o{}^2)} (\overline{n}_k^a + \frac{1}{2}) + \frac{\beta E^2}{2\Omega^2} [ -\alpha \sqrt{N} + \frac{2}{\sqrt{N}} \sum_k B^o(k) \frac{\pi}{\omega_k^o} (\overline{n}_k^o + \frac{1}{2}) \\ & + \frac{2}{\sqrt{N}} \sum_k B^a(k) \frac{\pi}{\omega_k^a} (\overline{n}_k^a + \frac{1}{2}) - \frac{4}{\sqrt{N}} \sum_k F(k) A(-k) \frac{\pi}{\omega_k^o (\omega_k^a{}^2 - \omega_k^o{}^2)} (\overline{n}_k^o + \frac{1}{2}) \\ & + \frac{4}{\sqrt{N}} \sum_k F(k) A(-k) \frac{\pi}{\omega_k^a (\omega_k^a{}^2 - \omega_k^o{}^2)} (\overline{n}_k^a + \frac{1}{2}) ]^2 \end{aligned} \quad (31)$$

Using equation (29), (31), the definition of the dielectric constant  $\epsilon$

$$(\epsilon - 1) = \frac{4\pi}{Nv} \frac{P}{E} \quad [v \text{ is the volume of the unit cell}] \quad (32)$$

and the average phonon occupation numbers [Eq. 23]

$$\bar{n}_k = \frac{1}{e^{\frac{\hbar\omega_k}{kT}} - 1} \quad (33)$$

one can write

$$\begin{aligned} \epsilon - 1 = & \frac{8\pi}{Nv} \sum_k |A(k)|^2 \frac{\hbar}{\omega_k^o(\omega_k^a - \omega_k^o)} \coth \frac{\hbar\omega_k^o}{2kT} - \frac{8\pi}{Nv} \sum_k |A(k)|^2 \frac{\hbar}{\omega_k^a(\omega_k^a - \omega_k^o)} \coth \frac{\hbar\omega_k^a}{2kT} \\ & + \frac{4\pi}{Nv} \frac{1}{\Omega^2} \left[ -a\sqrt{N} + \frac{1}{\sqrt{N}} \sum_k B^o(k) \frac{\hbar}{\omega_k^o} \coth \frac{\hbar\omega_k^o}{2kT} + \frac{1}{\sqrt{N}} \sum_k B^a(k) \frac{\hbar}{\omega_k^a} \coth \frac{\hbar\omega_k^a}{2kT} \right. \\ & \left. - \frac{2}{\sqrt{N}} \sum_k F(k) A(-k) \frac{\hbar}{\omega_k^o(\omega_k^a - \omega_k^o)} \coth \frac{\hbar\omega_k^o}{2kT} \right. \\ & \left. + \frac{2}{\sqrt{N}} \sum_k F(k) A(-k) \frac{\hbar}{\omega_k^a(\omega_k^a - \omega_k^o)} \coth \frac{\hbar\omega_k^a}{2kT} \right]^2 \end{aligned} \quad (34)$$

with

$$\Omega^2 = \frac{2}{N} \sum_k \frac{\pi}{\omega_k^0} G^0(k) \coth \frac{\hbar \omega_k^0}{2kT} + \frac{2}{N} \sum_k \frac{\pi}{\omega_k^a} G^a(k) \coth \frac{\hbar \omega_k^a}{2kT} \quad (35)$$

$$- \frac{2}{N} \sum_k |F(k)|^2 \frac{\pi}{\omega_k^0(\omega_k^a - \omega_k^0)} \coth \frac{\hbar \omega_k^0}{2kT} + \frac{2}{N} \sum_k |F(k)|^2 \frac{\pi}{\omega_k^a(\omega_k^a - \omega_k^0)} \coth \frac{\hbar \omega_k^a}{2kT} - \omega_0^2 .$$

If the deformation terms are absent, we obtain

$$\epsilon - 1 = \frac{4\pi(a^2/v)}{\Omega^2} . \quad (36)$$

In the classical limit of high temperature

$$\Omega^2 \sim (T - T_C) \quad (37)$$

and the dielectric constant follows a Curie-Weiss law.

$$\epsilon - 1 = \frac{C}{T - T_C} . \quad (38)$$

If the system does not spontaneously polarize at any positive temperature, it is then stabilized at  $T=0$  by zero point quantum mechanical fluctuations. The dielectric constant [Eq. 36] is independent of temperature in the vicinity of absolute zero. Note, however, that at intermediate temperatures the temperature dependence of the dielectric constant is in general different from the temperature dependence of Barrett's expression.<sup>9</sup>

This difference arises, since Barrett's calculation is based upon an Einstein model of the lattice and neglects the variation of lattice frequencies with wave vector.

In the classical limit, the dielectric constant with inclusion of the deformation terms [Eq. 34] can be written as

$$\epsilon - 1 = AT + \frac{C}{(T - T_C)} [1 + BT + DT^2] \quad . \quad (39)$$

A, B, C, D are temperature independent constants. The term linear in temperature appears since the presence of a second order electronic moment makes it possible for the field to drive modes other than the soft mode. This term should contribute a very small amount to the total dielectric constant. The presence of the higher order electronic moments also produces a temperature dependent Curie constant. The third order moment and the product of second order moment with the third order potential contribute to the linear temperature dependence of the Curie constant. The quadratic temperature dependent term involves the squares of the coupling coefficients appearing in the linear term. One can, therefore, conclude that the largest effect on the dielectric constant arising from the treatment of the deformation terms is to make the Curie constant vary linearly with temperature. At temperatures high compared with the Curie temperature, the dielectric constant [Eq. 39] can be written

$$\epsilon - 1 = \frac{C}{T - T_C} + F \quad . \quad (40)$$

Therefore, if one fits the temperature dependence of the dielectric constant with an expression of the form of equation(40) over a wide range of temperature above the Curie temperature, one cannot attribute

the value obtained for  $F$  solely to the presence of temperature independent infrared active modes. Electronic deformations may contribute significantly to this term.

In the preceding discussion we have treated the crystal as if it were clamped, i. e., we have neglected any effect due to thermal expansion. If one knows the pressure dependence of the dielectric constant, compressibility, and volume coefficient of thermal expansion, the temperature dependence of the dielectric constant of the material at fixed volume can be separated from the temperature dependence due to thermal expansion.<sup>12</sup> To obtain an accurate separation of the intrinsic temperature effect from this volume effect, these three quantities must be known over the range of temperatures for which the dielectric constant is measured. Such data is not available at present and, therefore, precludes the possibility of making an accurate comparison of our results with experiment.

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### 3. NONLINEAR DIELECTRIC CONSTANT

#### 3.1 Introduction

The connection between lattice dynamics and the dielectric properties of the hard ferroelectrics (e.g.  $\text{BaTiO}_3$  and isomorphs) has been made both theoretically<sup>1</sup> and experimentally<sup>2</sup>. It is now generally agreed that the interesting temperature dependent properties of ferroelectric materials arise from a long wavelength transverse optical mode which becomes unstable at the ferroelectric phase transition. Above the transition temperature the frequency of this long wavelength mode is not determined solely by harmonic interactions between the constituent ions. In fact, it appears that harmonic interactions are not sufficient to stabilize this mode and provide a real frequency above the transition temperature. The stabilization of this mode can be brought about by a consideration of anharmonic interactions<sup>3</sup>. Since anharmonic interactions perform such a fundamental role in providing for the stability of the system, they cannot be treated in the usual fashion<sup>4</sup> when one considers the statistical mechanical properties of a ferroelectric. That is to say, one cannot simply expand the free energy in powers of the anharmonic coupling coefficients. It has been shown however that one can do statistical theory for a ferroelectric by a simple modification of the usual procedure<sup>5</sup>. In reference 5 it was shown how one could obtain, in the language of Born-Von Karman lattice dynamics, the linear response of a ferroelectric above its transition temperature. In the present paper<sup>6</sup>, we consider in detail the nonlinear response.

In Section 3.2 the Hamiltonian we use is discussed. The Hamiltonian is a slightly modified version of the one treated by Szigeti<sup>7</sup> in discussing the temperature dependence of the dielectric constant of the alkali halides. One modification consists in including certain sixth-order anharmonic terms in the potential energy expansion. An additional difference is that all long wavelength transverse optical modes which are unstable in the harmonic approximation are collectively labeled with zero wave vector and assigned an imaginary frequency. An expression for



the temperature dependence of the nonlinear dielectric response above the transition temperature is then derived in Section 3.3. It will be shown in Section 3.4 that the temperature dependence of the nonlinear response we obtain is almost the same as obtained from the Devonshire phenomenological theory. The Devonshire theory was quite successful in describing the dielectric properties of  $\text{BaTiO}_3$  in its four phases with the use of one free energy function. As suggested by Anderson, the success of this procedure has its origin in the nature of the displacive transition. If only a small number of modes become unstable at the transition it can easily be shown why the same free energy function is valid both above and below the transition. This is discussed in Section 3.5. The deviations from the Devonshire theory could however be experimentally significant<sup>8</sup>. An order of magnitude estimate of the nonlinearity and a comparison with the measured value for  $\text{SrTiO}_3$  shows that it is reasonable to assume that anharmonic interactions are responsible for the observed nonlinearity<sup>9</sup>.

Thus it is seen that it is possible to systematically investigate the statistical mechanical properties of a ferroelectric material in terms of the Born-Von Karman lattice dynamics even though a small number of modes have imaginary frequencies in the harmonic approximation and that a lattice dynamical foundation of the Devonshire phenomenological theory can be exhibited.

### 3.2 Hamiltonian

We shall consider the following Hamiltonian:

$$\mathcal{H} = \mathcal{H}_1 - e^* EN^{\frac{1}{2}} q_0^0 + \mathcal{H}_2 + \mathcal{H}_3, \quad (1)$$

where

$$\begin{aligned}
 \mathcal{H}_1 = & -\frac{1}{2} \omega_0^{o2} q_0^{o2} + \frac{1}{2} \sum_k \omega_k^{o2} q_k^{o2} + \frac{1}{2} \sum_k \omega_k^{a2} q_k^{a2} \\
 & + N^{-\frac{1}{2}} q_0^o \sum_k A_k q_{-k}^o q_k^a \\
 & + N^{-1} F q_0^{o4} + N^{-1} q_0^{o2} \sum_k F_k q_k^{o2} + N^{-1} q_0^{o2} \sum_k G_k q_k^{a2},
 \end{aligned} \tag{2}$$

$$\begin{aligned}
 \mathcal{H}_2 = & E \sum_k X_k q_{-k}^o q_k^a \\
 & + EN^{-\frac{1}{2}} q_0^o \sum_k Y_k q_k^{o2} + EN^{-\frac{1}{2}} q_0^o \sum_k Z_k q_k^{a2},
 \end{aligned} \tag{3}$$

and

$$\begin{aligned}
 \mathcal{H}_3 = & N^{-2} G q_0^{o6} + N^{-2} q_0^{o4} \sum_k P_k q_k^{o2} + N^{-2} q_0^{o4} \sum_k Q_k q_k^{a2} \\
 & + N^{-1} q_0^{o2} \sum_k R_k q_k^{o4} + N^{-1} q_0^{o2} \sum_k S_k q_k^{a4} + N^{-1} q_0^{o2} \sum_k T_k q_{-k}^{o2} q_k^{a2}.
 \end{aligned} \tag{4}$$

The terms in the first line of Eq. (2) represent the harmonic part of the potential energy due to lattice displacements.  $q_0^o$  is the normal coordinate of that optical mode designated by zero wavenumber and which has a purely imaginary frequency associated with it. The specification of  $k = 0$  means that we consider a mode with wavelength long compared with the lattice parameter but small compared with the sample size. There are a large number of such modes<sup>10</sup>. However, they are only a very small fraction of the total number of modes and are therefore treated as a single mode.  $q_k^o$  and  $q_k^a$  are the normal coordinates of wave number  $k$  for the optical and acoustic mode, respectively. The second and third lines of Eq. (2) represent the third-and fourth-order anharmonic contributions to the potential energy, respectively.  $N$  is the number of ion pairs. The calculation is performed for two atoms per unit cell and the optical mode of this model is chosen as the soft temperature dependent ferroelectric mode. The second term on the right of Eq. (1) represents the first-order effect of the electronic distortions plus the effect of the displacement of the ions as a whole.  $E$  is the macroscopic electric field. The first and second lines of Eq. (3) are the second- and third-order effect of electronic deformations, respectively. Equation (4) represents the sixth-order anharmonic contribution to the potential energy. The remaining undefined quantities are constants. The summations over  $k$  are understood to be for all values of  $k$  different from zero. We have not explicitly included in the Hamiltonian terms arising from the kinetic energy since this will not contribute to the dielectric response. In this same vein, we shall neglect in the calculations that follow all multiplicative constants that do not effect the final result. The Hamiltonian has been simplified by the assumption of a cubic structure and a center of symmetry for the material under consideration. These assumptions concerning the structure are consistent with the perovskite structure in the unpolarized phase. All other terms in the Hamiltonian which have been neglected can be shown to make contributions smaller than the order of approximation to which we eventually work.

### 3.3 Dielectric Response Above the Transition Temperature

The work of the present section is divided into two parts. In Part A, we neglect the sixth-order anharmonic contributions to the Hamiltonian. This Hamiltonian then corresponds exactly with the one used previously<sup>5</sup> in obtaining an expression for the linear response. We exactly calculate the first two terms in a power series in  $E^2$  which represents the dielectric response. At temperatures well above the transition temperature the sixth-order anharmonicities can be shown to contribute relatively little to the nonlinear response<sup>11</sup> (their major effect is to introduce a term proportional to  $E^4$  in the dielectric response). This then is the reason we neglect them in this first part. In Part B we neglect the effect of electron deformations. The sixth-order anharmonicities are treated in a less exact way. The first three terms in a power series in  $E^2$  for the dielectric response are obtained. Below the transition the sixth-order anharmonicities are needed to stabilize the system. In a latter section we discuss the behavior below the transition. The results of this section will then be of great importance.

A.  $\mathcal{K}_3 = 0$

Our Hamiltonian consists of the first three terms of Eq. (1):

$$\mathcal{K}_A = \mathcal{K}_1 - e^* EN^{\frac{1}{2}} q_0^o + \mathcal{K}_2. \quad (5)$$

The partition function for this system is given by:

$$Z_A = \int_{-\infty}^{\infty} dq_0^o \int_{-\infty}^{\infty} \prod_k dq_k^o \int_{-\infty}^{\infty} \prod_k dq_k^a \exp \{ -\beta \mathcal{K}_A \}, \quad (6)$$

where  $\beta = 1/k_B T$ . The integrals over  $dq_k^o$  and  $dq_k^a$  may be readily performed.

In doing this, we make use of the following symmetry properties of the coefficients in the Hamiltonian:

$$\begin{aligned}
A_k &= -A_{-k}, & X_k &= -X_{-k} \\
\omega_k^{a2} &= \omega_{-k}^{a2}; & \omega_k^{o2} &= \omega_{-k}^{o2} \\
F_k &= F_{-k}; & G_k &= G_{-k} \\
Y_k &= Y_{-k}; & Z_k &= Z_{-k}.
\end{aligned}$$

Equation (6) then becomes

$$Z_A = \int_{-\infty}^{\infty} dq_0^o \prod_k \frac{1}{\sqrt{T_k(q_0^o)}} \exp \left\{ -\beta \left[ -\frac{1}{2} \omega_0^{o2} q_0^{o2} - e^* EN^{\frac{1}{2}} q_0^o + N^{-1} F q_0^{o4} \right] \right\}, \quad (7)$$

where

$$T_k(q_0^o) = a_k + \beta_k E + \gamma_k E^2 = a_k T'_k,$$

with

$$a_k = (1 + N^{-1} q_0^{o2} \mu_k) (1 + N^{-1} q_0^{o2} \lambda_k) - N^{-1} q_0^{o2} \nu_k$$

$$\beta_k = N^{-\frac{1}{2}} q_0^o \left[ \rho_k (1 + N^{-1} q_0^{o2} \lambda_k) + \sigma_k (1 + N^{-1} q_0^{o2} \mu_k) - 2\tau_k \sqrt{\nu_k} \right]$$

$$\gamma_k = N^{-1} q_0^{o2} \rho_k \sigma_k - \tau_k^2,$$

and

$$\mu_k = 2F_k / \omega_k^{o2}; \quad \rho_k = 2Y_k / \omega_k^{o2}$$

$$\lambda_k = 2G_k / \omega_k^{a2}; \quad \sigma_k = 2Z_k / \omega_k^{a2}.$$

(10)

$$\sqrt{\nu_k} = A_k / \omega_k^0 \omega_k^a; \quad \tau_k = X_k / \omega_k^0 \omega_k^a \quad (10)$$

Above the transition temperature, in the absence of the term quartic in  $q_0^0$ , the system described by Eq. (7) would be unstable if the anharmonic terms in the potential energy were neglected. That these terms do indeed stabilize the system is made evident by rewriting Eq. (7) in the following form:

$$Z_A = \int_{-\infty}^{\infty} dq_0^0 \prod_k \left[ \frac{1}{\sqrt{T_k(q_0^0)}} \exp \left\{ \frac{1}{2} N^{-1} q_0^{o2} (\lambda_k + \mu_k - \nu_k) \right\} \right] \times \exp \left\{ -\beta \left[ \frac{1}{2} \bar{\omega}_0^{o2} q_0^{o2} - e^* E N^{\frac{1}{2}} q_0^o + N^{-1} F q_0^{o4} \right] \right\} \quad (11)$$

where the "renormalized" frequency  $\bar{\omega}_0^0$  is proportional to  $\sqrt{T-T_c}$  and is thus real for  $T > T_c$ .  $\bar{\omega}_0^0$  is given by:

$$\bar{\omega}_0^{o2} = -\omega_0^{o2} + \frac{1}{N\beta} \sum_k (\lambda_k + \mu_k - \nu_k) \quad (12)$$

$T_c$  is a positive number (the Curie temperature) and can be obtained from Eq. (12). It is shown later [Eq. (17)] that the field independent parts of the product expression of Eq. (11) which are proportional to  $q_0^{o2}$  cancel. The  $N$  dependence of the remaining terms is such that they can in no way affect the stabilization of the system.

Since we wish to obtain an expression for the dielectric response (or the polarization) as a power series in  $E$ , we evaluate the expression for the partition as a power series in  $E$ .  $E$  is found in both the exponent and the function  $T_k$  of

Eq. (11). The expansion of the former is straightforward. The expansion of  $T_k^{-1}$  is also trivial. One must however then expand a function of the form  $\prod_k \{1 + A_k E + \dots\}$ . This can be accomplished by making use of the following result, the proof of which is easily given:

$$\begin{aligned}
 & \prod_k \{1 + A_k E + B_k E^2 + C_k E^3 + D_k E^4 + \dots\} \\
 &= 1 + E \left\{ \sum_k A_k \right\} + E^2 \left\{ \sum_k B_k + \sum_{k < k'} A_k A_{k'} \right\} \\
 &+ E^3 \left\{ \sum_k C_k + \sum_{k < k'} (A_k B_{k'} + A_{k'} B_k) + \sum_{k < k' < k''} A_k A_{k'} A_{k''} \right\} \\
 &+ E^4 \left\{ \sum_k D_k + \sum_{k < k'} (A_k C_{k'} + A_{k'} C_k + B_k B_{k'}) \right. \\
 &+ \sum_{k < k' < k''} (A_k A_{k'} B_{k''} + A_{k'} A_{k''} B_k + A_{k''} A_k B_{k'}) \\
 &+ \sum_{k < k' < k'' < k'''} A_k A_{k'} A_{k''} A_{k'''} \left. \right\} + \dots \\
 &= 1 + PE + QE^2 + RE^3 + SE^4 + \dots
 \end{aligned} \tag{13}$$

Upon making the necessary expansions, Eq. (11) then becomes:

$$\begin{aligned}
Z_A = & \int_0^\infty dq_0^0 \exp \{ -\beta \mathcal{K}_A' \} \prod_k \left[ \frac{1}{\sqrt{a_k}} \exp \left\{ \frac{1}{2} N^{-1} q_0^{o2} (\lambda_k + \mu_k - \nu_k) \right\} \right] \times \\
& \left[ 1 + E^2 \left\{ Q + P (\beta e^* N^{\frac{1}{2}} q_0^0) + \frac{1}{2} (\beta e^* N^{\frac{1}{2}} q_0^0)^2 \right\} \right. \\
& + E^4 \left\{ S + R (\beta e^* N^{\frac{1}{2}} q_0^0) + \frac{1}{2} Q (\beta e^* N^{\frac{1}{2}} q_0^0)^2 + \frac{1}{6} P (\beta e^* N^{\frac{1}{2}} q_0^0)^3 \right. \\
& \left. \left. + \frac{1}{24} (\beta e^* N^{\frac{1}{2}} q_0^0)^4 \right\} + \dots \right]
\end{aligned} \tag{14}$$

where  $\mathcal{K}_A' = \frac{1}{2} q_0^{o2} q_0^{o2} + N^{-1} F q_0^{o4}$ . The quantities P, Q, R, S are defined in terms of the  $A_k$ ,  $B_k$ ,  $C_k$ ,  $D_k$  by Eq. (7). The  $A_k$ ,  $B_k$ ,  $C_k$ ,  $D_k$  are given below:

$$\begin{aligned}
A_k &= -\frac{1}{2} N^{-\frac{1}{2}} q_0^0 \left[ I_k + N^{-1} q_0^{o2} II_k + 0 (N^{-2} q_0^{o4}) \right] \\
B_k &= -\frac{1}{2} III_k + N^{-1} q_0^{o2} \left[ \frac{3}{8} I_k^2 - \frac{1}{2} IV_k \right] + 0 (N^{-2} q_0^4) \\
C_k &= N^{-\frac{1}{2}} q_0^0 \left[ \frac{3}{4} I_k III_k + N^{-1} q_0^{o2} \left\{ -\frac{5}{16} I_k^3 + \frac{3}{4} (I_k IV_k + II_k III_k) \right\} \right. \\
&\quad \left. + 0 (N^{-2} q_0^{o4}) \right] \\
D_k &= \frac{3}{8} III_k^2 + N^{-1} q_0^{o2} \left[ \frac{9}{8} III_k IV_k - \frac{5}{16} I_k^2 III_k \right] + 0 (N^{-2} q_0^{o4}) .
\end{aligned} \tag{15}$$



where

$$\begin{aligned}
I_k &= \rho_k + \sigma_k - 2\tau_k \sqrt{\nu_k} \\
II_k &= (\rho_k \lambda_k + \sigma_k \mu_k) - (\lambda_k + \mu_k - \nu_k)(\rho_k + \sigma_k - 2\tau_k \sqrt{\nu_k}) \\
III_k &= -\tau_k^2 \\
IV_k &= \tau_k^2 (\lambda_k + \mu_k - \nu_k) + \rho_k \sigma_k
\end{aligned} \tag{16}$$

We have neglected the terms of odd power in  $E$  in Eq. (14) since these can be shown to be of odd power in  $q_0^0$  and hence vanish when the integral over  $q_0^0$  is evaluated. We have also changed the lower integration limit in Eq. (14) and continue to neglect unimportant multiplicative factors which make no contribution to the dielectric response. Before performing the integral in Eq. (14) a word should be said concerning the dependence upon  $N$  of our results (hence an explanation of the terms written as  $O(N^{-2} q_0^4)$  of Eq. (15)). The final quantity (the polarization) we will calculate must be proportional to  $N$ , which is a very large number. Thus in what follows, we neglect any contributions which are proportional to  $N^{-1}$  as compared to unity. Therefore we show explicitly only those terms which contribute to the desired  $N$ -dependence of the final result. One final step must be taken before we evaluate the integral. We must simplify the product expression in the integrand of Eq. (14). Bearing in mind our previous discussion about powers of  $N$ , this can be accomplished by use of a result equivalent to Eq. (13) [ $N^{-1}$  replaces  $E$  as the small parameter]. When this is carried out we find:

$$\prod_k \frac{1}{\sqrt{a_k}} \exp \left\{ \frac{1}{2} N^{-1} q_0^{o2} (\lambda_k + \mu_k - \nu_k) \right\}$$

$$= 1 + \frac{1}{4} N^{-1} r q_0^{o4} + o(N^{-2} q_0^{o6}) ; \quad (17)$$

$$r = N^{-1} \sum_k (\lambda_k^2 + \mu_k^2 + \nu_k^2 - 2\lambda_k \nu_k - 2\mu_k \nu_k) .$$

Substituting this and the values of P,Q,R,S gives for Eq. (14):

$$Z_A = 1 + E^2 \left\{ \frac{\int_0^\infty dq_0^o \exp(-\beta x_A') \left[ 1 + \frac{1}{4} N^{-1} r q_0^{o4} + o(N^{-2}) \right] \left[ N(a_0 + a_1 q_0^{o2}) + (a_2 q_0^{o2} + a_3 q_0^{o4}) + o(N^{-1}) \right]}{\int_0^\infty dq_0^o \exp(-\beta x_A') \left[ 1 + \frac{1}{4} N^{-1} r q_0^{o4} + o(N^{-2}) \right]} \right\} \quad (18)$$

$$+ E^4 \left\{ \frac{\int_0^\infty dq_0^o \exp(-\beta x_A') \left[ 1 + \frac{1}{4} N^{-1} r q_0^{o4} + o(N^{-2}) \right] \left[ N^2(b_0 + b_1 q_0^{o2} + b_2 q_0^{o4}) + N(b_3 + b_4 q_0^{o2} + b_5 q_0^{o4} + b_6 q_0^{o6}) + o(1) \right]}{\int_0^\infty dq_0^o \exp(-\beta x_A') \left[ 1 + \frac{1}{4} N^{-1} r q_0^{o4} + o(N^{-2}) \right]} \right\}$$

+ ... ,

where the  $a_i$  and  $b_i$  are constants (independent of  $q_0^0$  and  $N$ ) and can be obtained by directly comparing Eq. (18) with Eq. (14) and making use of Eqs. (13), (15) and (16). The integrals over  $dq_0^0$  are now readily performed. This is accomplished by making use of the following result:

$$\int_0^{\infty} dx x^{2n} \exp \{ -(ax^2 + \gamma x^4) \} \quad (19)$$

$$\cong a^{-n} \Gamma(n + \frac{1}{2}) [1 - \gamma a^{-2} (n + \frac{1}{2})(n + \frac{3}{2}) + O(\gamma^2)]$$

when  $\gamma a^{-1} < 1$ .

Thus we obtain the following expression for  $Z_A$ :

$$Z_A = 1 + NE^2 a + N^2 E^4 b + \dots, \quad (20)$$

where

$$a = (a_0 + \frac{1}{2a} a_1) + \frac{1}{N} \left[ -\frac{3\gamma}{4a^2} a_0 - \frac{15\gamma}{8a^3} a_1 + \frac{1}{2a} a_2 \right.$$

$$\left. + \frac{3}{4a^2} a_3 + \frac{3r}{16a^2} a_0 + \frac{15r}{32a^3} a_1 \right.$$

$$\left. - \left( \frac{3r}{16a^2} - \frac{3\gamma}{4a^2} \right) \left( a_0 + \frac{1}{2a} a_1 \right) \right] \quad (21)$$

$$\begin{aligned}
b = & (b_0 + \frac{1}{2a} b_1 + \frac{3}{4a^2} b_2) + \frac{1}{N} \left[ -\frac{3\gamma}{4a^2} b_0 - \frac{15\gamma}{8a^3} b_1 \right. \\
& - \frac{105\gamma}{16a^4} b_2 + b_3 + \frac{1}{2a} b_4 + \frac{3}{4a^2} b_5 + \frac{15}{8a^3} b_6 \\
& + \frac{3r}{16a^2} b_0 + \frac{15r}{32a^3} b_1 + \frac{105r}{64a^4} b_2 \\
& \left. - \left( \frac{3r}{16a^2} - \frac{3\gamma}{4a^2} \right) \left( b_0 + \frac{1}{2a} b_1 + \frac{3}{4a^2} b_2 \right) \right] ,
\end{aligned} \tag{21}$$

and

$$a = \frac{1}{2} \beta \bar{\omega}_\theta^2, \quad \gamma = \beta N^{-1} F.$$

The dielectric response is now obtained from Eq. (20) by means of the following definition:

$$\epsilon - 1 = \frac{P}{NE} = \frac{1}{N\beta E} \frac{\partial \ln Z}{\partial E}, \tag{22}$$

which gives

$$\epsilon - 1 = \{ 2\beta^{-1} a \} + \{ 4N\beta^{-1} (b - \frac{1}{2} a^2) \} E^2 + \dots \tag{23}$$

Instead of the definition of the dielectric response given by Eq. (22) we could have introduced the so-called differential dielectric response by

$$\epsilon - 1 = \frac{1}{N} \frac{\partial P}{\partial E} = \frac{1}{N\beta} \frac{\partial^2 \ln Z}{\partial E^2} \quad (24)$$

This does not change the first term on the right of Eq. (23) but would place a factor of three in front of the second term. In this section we continue to use the definition of the dielectric response given by Eq. (22).

That part of the dielectric response independent of  $E$  will be referred to as the linear dielectric response. All other terms, which depend on  $E$ , will be called the non-linear contribution to the dielectric response. The linear dielectric response for the Hamiltonian under consideration here, has been discussed in detail in reference 5. The result obtained here corresponds to the classical limit of their result [ their Eq. (39) ]. From Eq. (23) we directly obtain, neglecting all terms down by a factor of  $N^{-1}$  compared to unity:

$$\Gamma_{E^0}(\epsilon - 1) = AT + \frac{C}{T - T_c} (1 + BT + DT^2) \quad (25)$$

where by  $\Gamma_x(y)$  we mean that part of  $y$  proportional to  $x$  and where

$$\begin{aligned} A &= k_B \left[ \frac{1}{N} \sum_k \tau_k^2 \right] \\ B &= -k_B e^{*-1} \left[ \frac{1}{N} \sum_k (\rho_k + \sigma_k - 2\tau_k \sqrt{\nu_k}) \right] \\ C &= \frac{e^{*2}}{\omega_0^2} T_c \\ D &= \frac{1}{2} k_B^2 e^{*-2} \left[ \frac{1}{N^2} \sum_{k < k'} (\rho_k + \sigma_k - 2\tau_k \sqrt{\nu_k})(\rho_{k'} + \sigma_{k'} - 2\tau_{k'} \sqrt{\nu_{k'}}) \right] \end{aligned} \quad (26)$$

$$T_c = \omega_0^2 / k_B \left[ \frac{1}{N} \sum_k (\lambda_k + \mu_k - \nu_k) \right]. \quad (26)$$

We now write down the expression for that part of the non-linear response proportional to  $E^2$ . Note that since  $\epsilon - 1$  should not be proportional to  $N$ , one must worry about the factor of  $N$  in front of the second term on the right of Eq. (23). However, it is found that the terms independent of  $N$  in  $b - \frac{1}{2} a^2$  cancel exactly and that the lead contribution goes as  $N^{-1}$ , cancelling the factor of  $N$  in the appropriate term of Eq. (23). Thus we again obtain the proper dependence on  $N$  and our procedure is valid.

$$\begin{aligned} \Gamma_{E^2}(\epsilon - 1) = & A_1 T + \frac{T}{T - T_c} (B_0 + B_1 T) \\ & + \frac{T}{(T - T_c)^2} (C_0 + C_1 T + C_2 T^2) \\ & + \frac{T}{(T - T_c)^3} (D_0 + D_1 T + D_2 T^2 + D_3 T^3) \\ & + \frac{(E_0 + E_1 T)}{(T - T_c)^4} (F_0 + F_1 T + F_2 T^2 + F_3 T^3 + F_4 T^4). \end{aligned} \quad (27)$$

with

$$A_1 = k_B \left[ \frac{1}{N} \sum_k \Pi_k^2 \right]$$

$$B_0 = \frac{2k_B e^* T_c}{\omega_0^2} \left[ \frac{1}{N} \sum_k I_k \Pi_k \right]$$

$$B_1 = -\frac{k_B^2 T_c}{\omega_0^2} \left[ \frac{1}{N^2} \sum_{k < k'} I_k I_{k'} (\Pi_k + \Pi_{k'}) \right]$$

$$C_0 = \frac{2k_B e^* T_c^2}{\omega_0^4} \left[ \frac{1}{N} \sum_k \left( \frac{1}{2} I_k^2 - IV_k \right) \right] \quad (28)$$

$$C_1 = -\frac{2k_B^2 e^* T_c^2}{\omega_0^4} \left[ \frac{1}{N^2} \sum_{k < k'} \left\{ I_k \left( \frac{1}{2} I_{k'}^2 - IV_{k'} \right) + I_{k'} \left( \frac{1}{2} I_k^2 - IV_k \right) \right\} \right]$$

$$C_2 = \frac{k_B^3 T_c^2}{\omega_0^4} \left[ \frac{1}{N^3} \sum_{k < k' < k''} \left\{ I_k I_{k'} \left( \frac{1}{2} I_{k''}^2 - IV_{k''} \right) + I_{k'} I_{k''} \left( \frac{1}{2} I_k^2 - IV_k \right) \right. \right. \\ \left. \left. + I_k I_{k''} \left( \frac{1}{2} I_{k'}^2 - IV_{k'} \right) \right\} \right]$$

$$D_0 = -\frac{2k_B e^* T_c^3}{\omega_0^6} \left[ \frac{1}{N} \sum_k \Pi_k \right]$$

$$D_1 = \frac{3k_B^2 e^2 T_c^3}{\omega_0^6} \left[ \frac{1}{N^2} \sum_{k < k'} \left\{ I_k \Pi_{k'} + I_{k'} \Pi_k \right\} \right]$$

$$D_2 = - \frac{6k_B^3 e^3 T_c^3}{\omega_0^6} \left[ \frac{1}{N^3} \sum_{k < k' < k''} \left\{ I_k I_{k'} \Pi_{k''} + I_k I_{k''} \Pi_{k'} + I_{k'} I_{k''} \Pi_k \right\} \right]$$

$$D_3 = \frac{3k_B^4 T_c^3}{2\omega_0^6} \left[ \frac{1}{N^4} \sum_{k < k' < k'' < k'''} \left\{ I_k I_{k'} I_{k''} \Pi_{k'''} + I_k I_{k'} I_{k'''} \Pi_{k''} \right. \right. \\ \left. \left. + I_k I_{k''} I_{k'''} \Pi_{k'} + I_{k'} I_{k''} I_{k'''} \Pi_k \right\} \right]$$

$$E_0 = - \frac{1}{2} F$$

$$E_1 = \frac{1}{8} k_B r$$

$$F_0 = \frac{8e^4 T_c^4}{\omega_0^8}$$

$$F_1 = - \frac{16e^3 k_B T_c^4}{\omega_0^8} \left[ \frac{1}{N} \sum_k I_k \right]$$

$$F_2 = \frac{24e^2 k_B^2 T_c^4}{\omega_0^8} \left[ \frac{1}{N} \sum_{k < k'} I_k I_{k'} \right]$$

(28)



$$F_3 = - \frac{24e^* k_B^3 T_c^4}{\omega_0^8} \left[ \frac{1}{N^3} \sum_{k < k' < k''} I_k I_{k'} I_{k''} \right] \quad (28)$$

$$F_4 = \frac{12k_B^4 T_c^4}{\omega_0^8} \left[ \frac{1}{N^4} \sum_{k < k' < k'' < k'''} I_k I_{k'} I_{k''} I_{k'''} \right]$$

and where the  $I_k, II_k, III_k, IV_k$  are given by Eq. (16).

If electronic deformations are neglected, the only coefficients in Eq. (27) that do not vanish are  $E_0, E_1$  and  $F_0$ . Equation (27) for the non-linear response then becomes

$$\Gamma_{E^2}(\epsilon - 1) = \frac{(M + H' T)}{(T - T_c)^4} \quad (29)$$

where

$$M = E_0 F_0 = - \frac{4e^* k_B^4 T_c^4}{\omega_0^8} F \quad (30)$$

$$H' = E_1 F_0 = \frac{k_B e^* k_B^4 T_c^4}{\omega_0^8} r$$

From Eq. (27) it appears that the major effect of including the electronic deformations is to add a term  $E_0 F_1$  to  $H'$ . Then  $H'$  in Eq. (29) is replaced by  $H$  where

$$H = H' + \frac{8k_B e^* k_B^3 T_c^4}{\omega_0^8} F \left[ \frac{1}{N} \sum_k I_k \right] \quad (31)$$

$$\text{B. } \underline{\mathcal{K}_2 = 0}$$

The Hamiltonian we consider in this part is:

$$\mathcal{K}_B = \mathcal{K}_1 - e * EN^{\frac{1}{2}} q_0^o + \mathcal{K}_3. \quad (32)$$

We treat  $\mathcal{K}_3$  approximately ( $\mathcal{K}_1$  is sufficient to stabilize the system) and calculate only the lowest order effect of this term. In doing this we shall repeatedly make use of the following results:

$$\begin{aligned} (F; F_k; G_k) &\sim (A_k^2) \\ (G; P_k; Q_k; R_k; S_k; T_k) &\sim (F^2; F_k^2; G_k^2) \end{aligned} \quad (33)$$

By this we mean that any of the quantities on the left are of the same order of magnitude as any of the quantities on the right. That is to say, the fourth-order potential coefficients are the same order of magnitude as the square of the third-order potential coefficients etc. In this same vein we could also write:

$$\begin{aligned} (X_k) &\sim (A_k) \\ (Y_k, Z_k) &\sim (F, F_k, G_k) \end{aligned} \quad (34)$$

In what follows then, we neglect any terms whose magnitude is smaller than the sixth-order potential. Thus we will neglect terms which are proportional to  $GF$  etc.

The partition function for the system is given by Eq. (6) with  $\mathcal{K}_A$  replaced by  $\mathcal{K}_B$ . Denoting by  $\mathcal{K}_3'$  that part of  $\mathcal{K}_3$  which directly involves the  $q_k^o, q_k^a$  (i.e.  $\mathcal{K}_3' = \mathcal{K}_3 - N^{-2} G q_0^{o6}$ ) we simplify the calculation by writing

$$\exp \{-\beta \mathcal{H}_3'\} \approx 1 - \beta \mathcal{H}_3'.$$

The integrations over  $dq_k^0$  and  $dq_k^a$  in the partition function,  $Z_B$ , may then be performed in a straightforward manner. After this is done, again neglecting all unnecessary multiplicative factors, we find:

$$Z_B = \int_{-\infty}^{\infty} dq_0^0 \exp \left\{ -\beta \left[ -\frac{1}{2} \omega_0^2 q_0^2 - e^* EN^{\frac{1}{2}} q_0^0 + N^{-1} F q_0^2 + N^{-2} G q_0^6 \right] \right\} \times \quad (35)$$

$$\prod_k \left\{ \frac{1}{\sqrt{a_k}} \left[ 1 + \beta \left( N^{-1} \beta^{-2} q_0^2 u_k + N^{-2} \beta^{-1} q_0^4 v_k \right) \right] \right\},$$

where

$$u_k = -(3s_k + 3r_k + t_k) \quad (36)$$

$$v_k = -(q_k + p_k)$$

and

$$s_k = S_k / \omega_k^4; \quad r_k = R_k / \omega_k^2$$

$$t_k = T_k / \omega_k^2 \omega_k^2 \quad (37)$$

$$p_k = P_k / \omega_k^2; \quad q_k = Q_k / \omega_k^2$$

We now proceed as in Part A. To explicitly show the stabilization of the system above the transition temperature by the higher order potential energy terms, we remove from the product terms those contributions which depend on  $q_0^2$  and thus "renormalize" the frequency  $\omega_0^0$ . To within the approximation which we work, Eq. (35) is rewritten as below:

$$Z_B = \int_{-\infty}^{\infty} dq_0^o \exp \left\{ -\beta \left[ \frac{1}{2} \bar{\omega}_0^{o2} q_0^{o2} - e^* E N^{\frac{1}{2}} q_0^o + N^{-1} F q_0^{o4} + N^{-2} G q_0^{o6} \right] \right\} \times \quad (38)$$

$$\prod_k \left\{ \frac{1}{\sqrt{a_k}} \exp \left[ \frac{1}{2} N^{-1} q_0^{o2} (\lambda_k + \mu_k - \nu_k) \right] \right\} \prod_k \left\{ 1 + N^{-2} q_0^{o4} \nu_k \right\} ,$$

where the "renormalized" frequency  $\bar{\omega}_0^o$  is given by

$$\bar{\omega}_0^{o2} = -\omega_0^{o2} + \beta^{-1} \left[ \frac{1}{N} \sum_k (\lambda_k + \mu_k - \nu_k) \right] - 2\beta^{-2} \left[ \frac{1}{N} \sum_k u_k \right] . \quad (39)$$

Note that the renormalized frequency is proportional to  $-T_c + T + \sigma T^2$  ( $\sigma \ll 1$ ).

Both product terms of Eq. (38) are simplified as described previously. When this is done the second line of Eq. (38) is replaced by  $\{1 + \alpha N^{-1} q_0^{o4}\}$  where

$$\alpha = \frac{1}{4} r + \frac{1}{N} \sum_k \nu_k \quad (40)$$

and  $r$  is defined by Eq. (17). The partition function is finally written in the following form consistent with the previous approximation:

$$Z_B = \int_{-\infty}^{\infty} dq_0^o \exp \left\{ -\beta \left[ \frac{1}{2} \bar{\omega}_0^{o2} q_0^{o2} - e^* E N^{\frac{1}{2}} q_0^o + N^{-1} F q_0^{o4} \left( F - \frac{1}{\beta} \alpha \right) + N^{-2} q_0^{o6} G \right] \right\} . \quad (41)$$

The reason for writing  $Z_B$  in this form will be made evident in Section 3.5.

The partition function as given by Eq. (41) may now be directly evaluated. We again evaluate the partition function as a power series in even powers of  $E$  (the odd powers vanish identically). Since the renormalized frequency is positive, we

do not need the higher power terms in  $q_0^0$  (i.e.,  $\sim q_0^4, q_0^6$ ) in the exponent to stabilize the system so that in the evaluation of the integral we may treat them as perturbations.  $Z_B$  is then found to be of the same form as Eq. (20). However, we shall now calculate one additional term in this series. Therefore a term  $N^3 c E^6$  is added to the right of Eq. (20). The dielectric response is now obtained from Eqs. (22) and (23), the latter being modified by the addition of a term

$$\left[ 2\beta^{-1} N^2 (3c - 3ab + a^3) \right] .$$

Thus the dielectric response is written as

$$\epsilon - 1 = J + KE^2 + LE^4 + \dots \quad (42)$$

with

$$J = C/(T - T_c + \sigma T^2)$$

$$K = (M + H'' T)/(T - T_c + \sigma T^2)^4 \quad (43)$$

$$L = U/(T - T_c + \sigma T^2)^6 + V/(T - T_c + \sigma T^2)^7$$

and where

$$\sigma = -2k_B \left[ \frac{1}{N} \sum_k u_k \right] / \left[ \frac{1}{N} \sum_k (\lambda_k + \mu_k - \nu_k) \right] \quad (44)$$

$$H'' = 4a \frac{k_B e^{*4} T_c^4}{\omega_0^8}$$

$$U = -6G \frac{e^*{}^6 T_c^6}{\omega_0^{12}} \quad (44)$$

$$V = 48F \frac{e^*{}^6 T_c^7}{\omega_0^{14}}$$

$C$ ,  $T_c$  and  $M$  are defined in Eqs. (26) and (30). This result is exact to terms of order  $N^{-1}$ , that is, terms which vary as  $N^{-1}$  compared to unity are neglected. The point is again made that this result neglects contributions which involve any coefficient whose magnitude is smaller than the sixth-order anharmonic coupling coefficients.

### 3.4 Comparison with the Devonshire Theory

In the previous section we developed expressions for  $P$  (or equivalently  $\epsilon - 1$ ) as a series in powers of  $E$ . We now perform a simple inversion<sup>12</sup> of these series, that is, we express  $E$  as a series in powers of  $P$  so that the preceding results may be directly compared with the results of Devonshire's phenomenological theory. The discussion in this section is restricted to temperatures above the transition temperature.

Consider first the results of Section 3.3-A. Combining Eq. (25) and Eq. (29) with the modification as indicated by Eq. (31), the polarization may be written:

$$P = E \left\{ \epsilon_1 + \frac{C}{T - T_c} \right\} + E^3 \left\{ \frac{M + HT}{(T - T_c)^4} \right\} + \dots, \quad (45)$$

where the first term on the right of Eq. (45) has been simplified by neglecting the small term linear in the temperature and assuming  $T \gg T_c$  so that  $T/T - T_c \approx 1$ .

$\epsilon_1$  can now be assumed to consist of three parts; firstly, a contribution from the electronic polarizability and from the other hard modes which until now had been neglected and lastly, a contribution BC arising from the effect of electronic deformations. In Eq. (45) we have written  $p$  for  $N^{-1}P$ . Inverting Eq. (45) by a self consistent technique results in the following:

$$E = p \left\{ \epsilon_1 + \frac{C}{T - T_c} \right\}^{-1} - p^3 \left\{ \epsilon_1 + \frac{C}{T - T_c} \right\}^{-4} \left\{ \frac{M + HT}{(T - T_c)^4} \right\} + \dots \quad (46)$$

Equation (46) can be cast into the following form (again assuming  $T \gg T_c$ ):

$$E \approx p \left\{ \frac{1}{C} (-T_c + T + \bar{\sigma} T^2) \right\} - p^3 \left\{ \frac{1}{C^4} (M + \bar{H} T) \right\} + \dots \quad (47)$$

where

$$\begin{aligned} \bar{\sigma} &= -\frac{1}{C} \epsilon_1 \\ \bar{H} &= H - 4M \frac{\epsilon_1}{C} \end{aligned} \quad (48)$$

Let us now consider the results of Section 3.3-B. It follows from Eq. (43) that

$$E = p \left\{ \frac{1}{C} (-T_c + T + \sigma T^2) \right\} - p^3 \left\{ \frac{1}{C^4} (M + H'' T) \right\} - p^5 \frac{U}{C^6} + \dots \quad (49)$$

Combining the results of Eqs. (47) and (49) we conclude, that, to the order of approximation to which we work the result of considering the total Hamiltonian as given by Eq. (1) is an expression of the following form:

$$E = p \left\{ \frac{1}{C} (-T_c + T + \tilde{\sigma} T^2) \right\} - p^3 \left\{ \frac{1}{C^4} (M + \tilde{H} T) \right\} - p^3 \frac{U}{C^6} + \dots \quad (50)$$

where

$$\begin{aligned}\tilde{\sigma} &= \sigma + \bar{\sigma} \\ \tilde{H} &= \bar{H} + H'' - H' .\end{aligned}\tag{51}$$

A factor of  $H'$  has been subtracted from the right hand side of the equation defining  $\tilde{H}$  so that the contribution to  $\tilde{H}$  arising from the term proportional to  $r$  is not counted twice.

Thus both  $\tilde{\sigma}$  and  $\tilde{H}$  involve contributions from the electronic polarizability, the hard modes, the electronic deformations and the sixth-order potential energy terms.  $\tilde{H}$  also has a contribution which comes from the square of the fourth-order potential (i. e.,  $\sim r$  as given by Eq. (17)). We remark at this point that this result implies that in considering the linear response, if one writes the dielectric constant as

$$\epsilon - 1 = \epsilon_1 + \frac{C}{T - T_c} ,\tag{52}$$

that  $\epsilon_1$  involves contributions from the electronic polarizability, the hard modes, the electronic deformations and from the sixth-order potential energy terms. This point was considered previously in reference 5.

The expression for  $E$  vs  $P$  above the transition temperature can now be directly compared with the work of Devonshire. Devonshire writes an expression of the form of Eq. (50) but with  $\tilde{\sigma} = \tilde{H} = 0$ . Eq. (50) indicates that the result of the most general calculation would be of the form:

$$E = p \left\{ \sum_{n=0}^{\infty} a_n T^n \right\} + p^3 \left\{ \sum_{n=0}^{\infty} \beta_n T^n \right\} + p^5 \left\{ \sum_{n=0}^{\infty} \gamma_n T^n \right\} + \dots\tag{53}$$

That the terms involving  $\tilde{\sigma}$  and  $\tilde{H}$  are not negligible and may indeed be experimentally observed will be discussed in Section 3.6. Corrections to the Devonshire theory as proposed here have previously been considered by Triebwasser<sup>8</sup> and by Kozlovski<sup>13</sup>.



### 3.5 Dielectric Response Below the Transition Temperature

Up to this point, we have assumed that the temperature was above transition temperature. It is known, however, that even below the transition temperature an expression of the form given by Eq. (50) or Eq. (53) can be used to explain the observed dielectric response. We now wish to briefly indicate how this follows directly from the lattice dynamics of the problem. In what follows we shall neglect the effect of electronic deformations so that we again consider the Hamiltonian as given by Eq. (32). We work to the same degree of approximation as discussed previously. We further assume that, although this Hamiltonian was derived under the assumption of certain symmetry conditions (Section 3.2) which are no longer strictly valid below the transition, the form of the Hamiltonian is the same.<sup>1</sup>

When  $T < T_c$ , the square of the renormalized frequency  $\bar{\omega}_0^2$  is no longer positive and the system again appears to be unstable. Further, terms of the form  $N^{-1}Fq_0^{o4}$  ( $F > 0$ ) are also unable to stabilize the system since due to electrostrictive effects<sup>3</sup>  $F \rightarrow F' < 0$ . Thus it is left to terms of the form  $N^{-2}Gq_0^{o6}$  ( $G > 0$ ) arising from the sixth-order anharmonic potential energy to stabilize the system. Thus the thermodynamic treatment of this section must differ fundamentally from that of the previous sections.

The reason for rewriting the partition function  $Z_B$  in the form given by Eq. (41) will now be made evident. We may look upon the factor multiplying  $-\beta$  in the exponential of Eq. (41) as an effective Hamiltonian (the system being stabilized by the term  $N^{-2}Gq_0^{o6}$ ). Below the transition temperature the polarization is directly related to the displacements  $q_0^o$  so that we may again simply obtain an expression for  $E$  vs  $P$ . From Eq. (41) we have:

$$\mathcal{H}_{\text{eff}} = \frac{1}{2} \bar{\omega}_0^2 q_0^{o2} - e^* E N^{\frac{1}{2}} q_0^o + N^{-1} q_0^{o4} (F - \alpha \beta^{-1}) + N^{-2} q_0^{o6} G + \dots \quad (54)$$

If the system is in equilibrium the free energy must be a minimum,

$$\frac{\partial \mathcal{K}_{\text{eff}}}{\partial q_0^0} = 0. \quad (55)$$

In essence, we evaluate the partition function by means of the method of steepest descents. Equation (55) then defines the saddle point. Substituting Eq. (54) in Eq. (55) then gives

$$e^* EN^{\frac{1}{2}} = \omega_0^2 q_0^0 + 4N^{-1} q_0^0 (F - \alpha\beta^{-1}) + N^{-2} q_0^0 G + \dots \quad (56)$$

It can be simply shown that

$$p = N^{-1}P = e^* N^{-\frac{1}{2}} q_0^0, \quad (57)$$

so that we have

$$E = p \left\{ \omega_0^2 e^{*-2} \right\} + p^3 \left\{ 4e^{*-4} (F - \alpha\beta^{-1}) \right\} + p^5 \left\{ 6e^{*-6} G \right\} + \dots \quad (58)$$

which is identical to Eq. (50). It thus appears that the basic reason that one free energy function works both above and below the transition temperature is intimately related to the fact that we have considered only a single unstable mode and that the other modes remain unchanged.

### 3.6 Conclusion

It has been shown how one can obtain an expression for the nonlinear response of a ferroelectric in terms of the coupling parameters of the Born-VonKarman lattice dynamical theory. Up to the present all other calculations along these lines have been essentially single particle calculations and have hence neglected certain

contributions made manifest by the lattice dynamical treatment. The role of electron cloud deformations has also been investigated and shown to contribute to the temperature dependence of the nonlinear response. It has also been shown how the assumption of one unstable mode used in conjunction with the same Hamiltonian both above and below the transition is equivalent to Devonshire's assumption that one phenomenological free energy function suffices to describe the behavior both above and below the transition. Only order of magnitude estimates are possible at present to justify the origin of the observed effects. The detailed calculation that has been presented is of interest however, since the quantities involved also have implications for the observed optical behavior of ferroelectric materials. Indeed, as Szigetti has pointed out, widths of absorption bands, the presence of sidebands, etc, are determined by essentially the same coupling parameters that are involved in the temperature dependence of the dielectric response.

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#### **4. ELECTROSTRICTIVE CONSTANTS OF FERROELECTRIC MATERIALS**

##### **4.1 Introduction**

The piezoelectric coefficients have been related to the microscopic properties of the crystalline lattice by Born and Huang in their classic text on lattice dynamics.<sup>1</sup> This theory is applicable when the induced stress in a material is proportional to the applied field. If however, every atom in the lattice is at a center of symmetry, this linear effect is absent and the stress is proportional to the square of the field. In this paper it will be shown how one can relate this quadratic behavior to the microscopic properties of the lattice. The quadratic dependence of stress on field has been called electrostriction by a number of investigators and this is the terminology that will be adopted here.

Electrostrictive effects are generally small and difficult to measure in most materials. Ferroelectrics however exhibit pronounced electromechanical behavior. These materials undergo a transition to a polarized phase below a certain temperature. Above the transition temperature they are paraelectric, with a large dielectric constant which obeys a curve Weiss law. One may classify these materials as belonging to one of two categories;<sup>2</sup> those that are piezoelectric in the unpolarized phase and those that are electrostrictive in the unpolarized phase. The piezoelectric ferroelectrics have been recently discussed by Cochran<sup>3</sup> and will not concern us in the present work. Barium titanate and its isomorphs belong to the second category since in their high temperature cubic phase each ion is at a center of symmetry. The electrostrictive properties of these materials are of interest for several reasons. It appears that the explanation of the observed first order phase transition in  $\text{BaTiO}_3$  requires the presence of suitable electrostrictive terms in the expression for the free energy of the material.<sup>4</sup> Electrostrictive behavior also leads to the difference between the value of the clamped and free nonlinear dielectric constant in the paraelectric phase.<sup>5</sup> One pertinent assumption of Devonshire's theory,<sup>4</sup> is that the piezoelectric coefficients obtained for the material in the polarized phase are related simply to the

electrostrictive coefficients of the material in the unpolarized phase. The microscopic basis for such assumption has been discussed by Anderson.<sup>6</sup> In this sense one could therefore say that the electromechanical behavior of barium titanate in all phases is electrostrictive.

The calculation relating the electrostrictive coefficients to the microscopic coupling parameters of the lattice also presents some new and interesting problems not encountered in the linear theory. Toupin has stated that in general one cannot consider the stress tensor as a polynomial in the electric field and elements of infinitesimal strain measure.<sup>7</sup> He has demonstrated that this assumption violates the invariance of the stored energy to rigid rotations. To the order we will work, however, it will not be necessary to augment the strain tensor with an antisymmetric part representing rotations in the medium. We can forego this complication since we treat a lattice in which each atom is at a center of symmetry. It should therefore be emphasized that the expressions obtained for the electrostrictive coefficients in this paper are not valid for the quadratic response of a material which also exhibits a linear response. Toupin also raises the following interesting point. If the electric field and polarization are not parallel to each other, the Maxwell stress tensor in the dielectric medium is not symmetric. Hence if the medium is to be in static equilibrium there must be an additional stress system whose antisymmetric part is equal and opposite to the antisymmetric part of the Maxwell stress tensor. One can call these additional stresses, local stresses. In the calculation presented in Section 4.2 it will be shown that Maxwell stresses and local stresses can be identified and that both are in static equilibrium with each other.

It might appear at first that in order to calculate an effect that is quadratic in the macroscopic field one would need to work within the framework of the theory of finite elasticity. This, however is not necessary since even though the macroscopic field depends on the ionic displacements, it also depends on the geometry

of the sample through the depolarization factor and therefore the field and displacement are independent quantities. One can therefore work to any given order in each independently.

#### 4.2 Electrostrictive Constants

Expressions for the electrostrictive constants are obtained after a comparison has been made between the macroscopic and microscopic theories. In this section we will therefore consider the elastic equation of motion for an electrostrictive medium and the microscopic lattice equations of motion. These equations will be put into a form which will facilitate a comparison between them. The elastic equation of motion is

$$\rho \ddot{u}_a = \sum_v \frac{\partial S_{av}}{\partial X_v} \quad (1)$$

$\rho$  is the mass density of the medium.  $u_a$  is the  $a$  component of the displacement in the medium.  $S_{av}$  is the  $av$ <sup>th</sup> component of the stress tensor.  $X_v$  is the  $v$ <sup>th</sup> component of a general point in the medium.

The constitutive relation between stress, strain and field is

$$S_{av} = \sum_{\delta, \Delta} C_{av, \delta\Delta} s_{\delta\Delta} + \sum_{\delta, \Delta} d_{av, \delta\Delta} E_{\delta} E_{\Delta} \quad (2)$$

We assume that the piezoelectric effect is absent since each ion is considered to be at a center of symmetry. The  $C_{av, \delta\Delta}$  and  $d_{av, \delta\Delta}$  are the elastic constants and electrostrictive constants respectively.  $E_{\delta}$  is the  $\delta$ <sup>th</sup> component of the macroscopic field.  $s_{\delta\Delta}$  is the  $\delta\Delta$ <sup>th</sup> component of the strain tensor which is related to the displacement gradients as follows.

$$\epsilon_{\delta\Delta} = \frac{1}{2} \left( \frac{\partial u_{\delta}}{\partial X_{\Delta}} + \frac{\partial u_{\Delta}}{\partial X_{\delta}} \right) \quad (3)$$

Substituting Eq. (2) and Eq. (3) into Eq. (1) we obtain

$$\rho \ddot{u}_a = \sum_{\nu, \delta, \Delta} C_{a\nu, \delta\Delta} \frac{\partial^2 u_{\delta}}{\partial X_{\nu} \partial X_{\Delta}} + 2 \sum_{\nu, \delta, \Delta} d_{a\nu, \delta\Delta} E_{\Delta} \frac{\partial E_{\delta}}{\partial X_{\nu}} \quad (4)$$

The symmetry of the elastic and electrostrictive constants have been used to obtain this result. The displacements and macroscopic field are now Fourier analyzed.

$$u_a = \int d\bar{y} u_{a\bar{y}} e^{2\pi i \bar{y} \cdot \bar{r}} \quad (5)$$

$$E_{\delta} = \int d\bar{y} E_{\delta\bar{y}} e^{2\pi i \bar{y} \cdot \bar{r}} \quad (6)$$

If Eq. (5) and (6) are substituted into Eq. (4) and the usual manipulations performed to obtain uncoupled motion in the harmonic approximation, one obtains

$$\begin{aligned} \rho \ddot{u}_{a\bar{y}} = & 4\pi^2 \sum_{\nu, \delta, \Delta} C_{a\nu, \delta\Delta} y_{\nu} y_{\Delta} u_{\delta\bar{y}} \\ & + 4\pi i \sum_{\nu, \delta, \Delta} d_{a\nu, \delta\Delta} \iint d\bar{y}' d\bar{y}'' E_{\delta\bar{y}'} E_{\Delta\bar{y}''} y_{\nu}' \delta(\bar{y}' + \bar{y}'' - \bar{y}) \end{aligned} \quad (7)$$



$\delta(\bar{y})$  is the Dirac delta function. It is seen from Eq. (7) that modes of wave vector  $\bar{y}$  are no longer uncoupled. Different modes are coupled due to the presence of the electrostrictive term. We will obtain expressions for the electrostrictive constants from a comparison of Eq. (7) with the microscopic equations of motion. Therefore we turn to an examination of the microscopic equations of motion. In what follows, the rigid ion model is used for simplicity. The generalization to more sophisticated models within the adiabatic approximation should be straightforward.

The lattice equation of motion in the notation of Born and Huang is

$$m_k \ddot{u}_a^{(l)}(k) = - \sum_{l', k', \beta} \phi_{a\beta}^{(l, l')}(k, k') u_{\beta}^{(l')}(k') + q_k \epsilon_a - \frac{1}{2} \sum_{\substack{l', k', \beta \\ l'', k'', \gamma}} \phi_{a\beta\gamma}^{(l, l', l'')}(k, k', k'') u_{\beta}^{(l')}(k') u_{\gamma}^{(l'')}(k'') \quad (8)$$

$m_k$  is the mass of the  $k^{\text{th}}$  type atom.  $u_a^{(l)}(k)$  is the  $a^{\text{th}}$  component of the displacement of the  $k^{\text{th}}$  type atom in the  $l^{\text{th}}$  cell. The  $\phi_{a\beta}$  and  $\phi_{a\beta\gamma}$  are second and third order coupling coefficients respectively.  $q_k$  is the ionic charge of the  $k^{\text{th}}$  type atom.  $\epsilon_a$  is the  $a^{\text{th}}$  component of the macroscopic field. The harmonic interaction has been split up into a short and long range part as discussed by Born and Huang. The macroscopic field  $\epsilon$  therefore includes contributions from the long range interaction between ions and  $\phi_{a\beta}$  is determined by the short range interactions between ions.

After application of

$$w_a(\vec{k}) = \frac{1}{\sqrt{N}} \sum_{\vec{y}} w_a(\vec{k}|\vec{y}) e^{2\pi i \vec{y} \cdot \vec{x}(\vec{k})} \quad (9)$$

with

$$w_a(\vec{k}) = \sqrt{m_k} u_a(\vec{k}) \quad (10)$$

the equation of motion Eq. (8) can be written in the following form.

$$\ddot{w}_a(\vec{k}|\vec{y}) = - \sum_{m, k', \beta} D_{a\beta}(\vec{k}|\vec{k}') e^{2\pi i \vec{y} \cdot \vec{x}(\vec{k}'|\vec{k})} w_\beta(\vec{k}'|\vec{y}) + \frac{q_k}{\sqrt{m_k}} \epsilon_{a\vec{y}} \quad (11)$$

$$- \frac{1}{2\sqrt{N}} \sum_{\vec{y}', \vec{y}''} \sum_{m, k', \beta} D_{a\beta\gamma}(\vec{k}|\vec{k}'|\vec{k}'') w_\beta(\vec{k}'|\vec{y}') w_\gamma(\vec{k}''|\vec{y}'') e^{2\pi i [\vec{y}' \cdot \vec{x}(\vec{k}'|\vec{k}) + \vec{y}'' \cdot \vec{x}(\vec{k}''|\vec{k})]} \Delta(\vec{y}' + \vec{y}'' - \vec{y})$$

where we have set

$$D_{a\beta}(\vec{k}|\vec{k}') = \frac{1}{(m_k m_{k'})^{1/2}} \phi_{a\beta}(\vec{k}|\vec{k}') \quad (12)$$

$$D_{a\beta\gamma}(\vec{k}|\vec{k}'|\vec{k}'') = \frac{1}{(m_k m_{k'} m_{k''})^{1/2}} \phi_{a\beta\gamma}(\vec{k}|\vec{k}'|\vec{k}'') \quad (13)$$

$$\epsilon_{\alpha\bar{y}} = -\frac{4\pi}{v_a} \left( \frac{y_a}{|\bar{y}|} \right) \sum_{\beta} \left( \frac{y_{\beta}}{|\bar{y}|} \right) \sum_{k'} \frac{q_{k'}}{\sqrt{m_{k'}}} w_{\beta}(k' | \bar{y}) \quad (14)$$

$$\Delta(\bar{y}' + \bar{y}'' - \bar{y}) = 1 \quad \text{for } \bar{y}' + \bar{y}'' - \bar{y} = 0 \text{ or a reciprocal lattice vector.} \quad (15)$$

$$= 0 \quad \text{all other values of } \bar{y}', \bar{y}'', \text{ and } \bar{y}$$

One method of identifying the electrostrictive coefficients in Eq. (7) with the microscopic parameters of Eq. (11) is the following. Let us assume that up to time zero, the nonlinear interactions in both of these equations are not present. At time zero they are instantaneously switched on. The displacements are set equal to unperturbed displacements plus small connections due to the presence of the nonlinear interactions. We will treat Eq. (11) first. Set

$$w_{\alpha}(k|\bar{y}) = w_{\alpha 0}(k|\bar{y}) + v_{\alpha}(k|\bar{y}) \quad (16)$$

Subscript zero refers to the displacements in the absence of the third order anharmonic coupling parameter. For an infinitesimal time after the anharmonic interaction has been turned on, we may write.

$$\ddot{w}_{\alpha 0}(k|\bar{y}) = - \sum_{m, k', \beta} D_{\alpha\beta} \binom{-m}{k \ k'} e^{2\pi i \bar{y} \cdot \bar{x} \binom{m \ 0}{k' \ k}} w_{\beta}(k' | \bar{y}) + \frac{q_k}{\sqrt{m_k}} \epsilon_{\alpha\bar{y}} \quad (17)$$

$$\ddot{v}_{\alpha}(k|\bar{y}) = -\frac{1}{2\sqrt{N}} \sum_{\bar{y}' \bar{y}''} \sum_{\substack{m \ k' \ \beta \\ n \ k'' \ \gamma}} D_{\alpha\beta\gamma} \binom{0 \ m \ n}{k \ k' \ k''} w_{\beta}(k' | \bar{y}') w_{\gamma}(k'' | \bar{y}'') e^{2\pi i [\bar{y}' \cdot \bar{x} \binom{m \ 0}{k' \ k} + \bar{y}'' \cdot \bar{x} \binom{n \ 0}{k'' \ k}]} \quad (18)$$

$$\Delta(\bar{y}' + \bar{y}'' - \bar{y})$$

The elastic Eq. (7) can be treated in a similar fashion. The displacement  $u_{a\bar{y}}$  is set equal to an unperturbed part plus a small correction

$$u_{a\bar{y}} = u_{oa\bar{y}} + v_{a\bar{y}} \quad (19)$$

In the same spirit in which Eq. (17) and (18) have been written we write

$$\rho \ddot{u}_{oa\bar{y}} = -4\pi^2 \sum_{\nu, \delta, \Delta} C_{a\nu, \delta\Delta} y_{\nu} y_{\Delta} u_{\delta\bar{y}} \quad (20)$$

$$\rho \ddot{v}_{a\bar{y}} = 4\pi i \sum_{\nu, \delta, \Delta} d_{a\nu, \delta\Delta} \iint d\bar{y} d\bar{y}' E_{\delta\bar{y}} E_{\Delta\bar{y}'} y'_{\nu} \delta(\bar{y}'' + \bar{y}' - \bar{y}) \quad (21)$$

Equations (17) and (20) are just the equations that Born and Huang use to obtain expressions for the elastic constants. Had we included the piezoelectric terms in Eq. (20); these equations could be used to determine expressions for the piezoelectric coefficients also. To obtain expressions for the electrostrictive coefficients we must compare Eq. (18) with (21). Before this comparison is possible however, Eq. (18) must be written in the limit of long waves; the quadratic dependence on the macroscopic field must be exhibited; the center of mass motion for the unit cell must be obtained. In what follows we describe in some detail how this is done.

To obtain the motion of the center of mass of the unit cell we multiply both sides of Eq. (18) by  $\sqrt{m_k}$ , sum over the contents of the unit cell and divide by the sum of the masses in the unit cell.

o

$$V_a(\bar{y}) = \frac{\sum_k \sqrt{m_k} \ddot{v}_a(k|\bar{y})}{\sum_k m_k}$$

$$= - \frac{1}{2\sqrt{N}} \frac{1}{\sum_k m_k} \sum_{y', y''} \sum_{\substack{mk'\beta \\ nk''\gamma}} \sqrt{m_k} D_{a\beta\gamma} \binom{0mn}{kk'k''} w_{o\beta}(k'|\bar{y}') w_{o\gamma}(k''|\bar{y}'') e^{2\pi i [\bar{y} \cdot \bar{x}_{k'k}^{(mo)} + \bar{y}'' \cdot \bar{x}_{k''k}^{(n0)}]} e^{2\pi i [\bar{y} + \bar{y}'' - \bar{y}]} \quad (22)$$

For wavelengths large compared with the atomic interaction distance, the exponential in Eq. (22) is expanded.

$$e^{2\pi i [\bar{y} \cdot \bar{x}_{k'k}^{(mo)} + \bar{y}'' \cdot \bar{x}_{k''k}^{(n0)}]} = 1 + 2\pi i [\bar{y} \cdot \bar{x}_{k'k}^{(mo)} + \bar{y}'' \cdot \bar{x}_{k''k}^{(n0)}] + \dots \quad (23)$$

The first term in this expansion appearing on the right of Eq. (22) is

$$= \frac{1}{2\sqrt{N}} \frac{1}{\sum_k m_k} \sum_{y', y''} \sum_{\substack{mk'\beta \\ nk''\gamma}} \sqrt{m_k} D_{a\beta\gamma} \binom{0mn}{kk'k''} w_{o\beta}(k'|\bar{y}') w_{o\gamma}(k''|\bar{y}'') \Delta(\bar{y} + \bar{y}'' - \bar{y}) \quad (24)$$

and this term vanishes due to the following translational invariance condition

$$\sum_{m, k} \phi_{a\beta\gamma} \binom{0mn}{kk'k''} = 0 \quad (25)$$

Contributions to Eq. (22) from the next term in the expansion do not vanish, and we therefore write

$$\ddot{v}_a(\bar{y}) = -\frac{\pi i}{\sqrt{N}} \sum_k \frac{1}{m_k} \sum_{y', y''} \sum_{\substack{mk' \beta \\ nk'' \gamma}} \sqrt{m_k} D_{a\beta\gamma} \begin{pmatrix} 0 & m & n \\ k & k' & k'' \end{pmatrix} w_{0\beta}(k'|\bar{y}') w_{0\gamma}(k''|\bar{y}'') [\bar{y} \cdot \bar{x}_{(k'k)}^{(m0)} + \bar{y}'' \cdot \bar{x}_{(k''k)}^{(n0)}] \Delta(\bar{y}' + \bar{y}'' - \bar{y}) \quad (26)$$

If the following interchanges are performed in the term arising from the second quantity in the square brackets

$$\bar{y}' \rightleftharpoons \bar{y}'', m \rightleftharpoons n, k' \rightleftharpoons k'', \beta \rightleftharpoons \gamma$$

we can write

$$\ddot{v}_a(\bar{y}) = -\frac{2\pi i}{\sqrt{N}} \sum_k \frac{1}{m_k} \sum_{y', y''} \sum_{\substack{mk' \beta \\ nk'' \gamma}} \sqrt{m_k} D_{a\beta\gamma} \begin{pmatrix} 0 & m & n \\ k & k' & k'' \end{pmatrix} w_{0\beta}(k'|\bar{y}') w_{0\gamma}(k''|\bar{y}'') y' \cdot \bar{x}_{(k'k)}^{(m0)} \Delta(\bar{y}' + \bar{y}'' - \bar{y}) \quad (27)$$

Let us next decompose the displacements into the normal modes

$$w_{0a}(k|\bar{y}) = \sum_j \epsilon_a(k|j) Q(j) \quad (28)$$

The equation of motion for the  $Q(j)$  are

$$\ddot{Q}(j) + \omega^2(j) Q(j) = \sum_{k, a} \epsilon_a^*(k|j) \frac{q_k}{\sqrt{m_k}} E_a(\bar{y}) \quad (29)$$

We can write

$$Q(\bar{y}) = q(\bar{y}) + \sum_{k, a} \epsilon_a^*(k|\bar{y}) \frac{q_k}{\sqrt{m_k}} \epsilon_a(\bar{y}) / \omega^2(\bar{y}) \quad (30)$$

where  $q(\bar{y})$  is the solution of

$$\ddot{q}(\bar{y}) + \omega^2(\bar{y}) q(\bar{y}) = 0 \quad (31)$$

Substituting (28) and (30) into (27) we obtain

$$\begin{aligned} \ddot{v}_a(\bar{y}) = & -\frac{2\pi i}{\sqrt{N}} \sum_k \frac{1}{m_k} \sum_{y', y''} \sum_{j' j''} \sum_{mk' \beta} \sum_{nk'' \gamma} \sum_{k''', \delta} D_{a\beta\gamma} \epsilon_{\delta}^{*}(k''' | j_1^0) \epsilon_{\beta}(k' | j_1^0) \\ & \times \frac{\epsilon_{\Delta}^{*}(k'' | j_n^0) \epsilon_{\gamma}(k'' | j_n^0)}{\omega^2(j_n^0)} \\ & \times \frac{q_{k'''} q_{k''''}}{\sqrt{m_{k'''} m_{k''''}}} \bar{y}^i \cdot \bar{x} \left( \frac{m_0}{k' k} \right) \epsilon_{\delta}(\bar{y}') \epsilon_{\Delta}(\bar{y}'') \Delta(\bar{y}' + \bar{y}'' - \bar{y}) \end{aligned} \quad (32)$$

Finally, the Kronecher delta function goes over to a Dirac delta function in the limit of infinite periodicity volume.

$$\Delta(\bar{y}) \rightarrow \frac{1}{N v_a} \delta(\bar{y}) ; \quad \sum_{\bar{y}} \rightarrow N v_a \int d\bar{y}$$

We obtain

$$\ddot{v}_{ay} = -\frac{2\pi i}{\rho v_a} \iint d\tilde{y}' d\tilde{y}'' \sum_{j', j''} \sum_{mk'\beta} \sum_{nk''\gamma} \sum_k D_{\alpha\beta\gamma} \binom{omn}{kk'k''} \frac{\epsilon_{\delta}^*(k^m | j') \epsilon_{\beta}(k' | j')}{\omega_{(j')}^2} \frac{\epsilon_{\Delta}^*(k^m | j'') \epsilon_{\gamma}(k'' | j'')}{\omega_{(j'')}^2} \quad (33)$$

$$\times \sqrt{\frac{m_k}{m_{k^m} m_{k^m}}} q_{k^m} q_{k^m} \tilde{y}' \cdot \tilde{X} \binom{m o}{k' k} E_{\delta\tilde{y}'} E_{\Delta\tilde{y}''} \delta(\tilde{y}' + \tilde{y}'' - \tilde{y})$$

where use has been made of

$$v_{ay} = \sqrt{N} v_a v_a(\tilde{y}) \quad (34)$$

$$E_{ay} = \sqrt{N} v_a E_a(\tilde{y})$$

$v_a$  is the volume of the unit cell.

Equation (33) can now be compared directly with Eq. (21) and the following expression obtained for the electrostrictive coefficients

$$d_{av, \delta\Delta} = \frac{1}{2v_a} \sum_{j', j''} \sum_{mk'\beta} \sum_{nk''\gamma} \sum_k D_{\alpha\beta\gamma} \binom{omn}{kk'k''} \frac{\epsilon_{\delta}^*(k^m | j') \epsilon_{\beta}(k' | j')}{\omega_{(j')}^2} \frac{\epsilon_{\Delta}^*(k^m | j'') \epsilon_{\gamma}(k'' | j'')}{\omega_{(j'')}^2} \quad (35)$$

$$\times \sqrt{\frac{m_k}{m_{k^m} m_{k^m}}} q_{k^m} q_{k^m} X_v \binom{o m}{k k'}$$

These coefficients are subject to the following symmetry relations

$$d_{av, \delta\Delta} = d_{va, \delta\Delta} = d_{av, \Delta\delta} \quad (36)$$

and in general there are thirty-six independent constants.



As we have mentioned in the introduction, Toupin<sup>7</sup> has pointed out the following interesting fact. If the electric field and polarization in a medium are not parallel to each other, the Maxwell stress tensor in the dielectric medium is not symmetric. Hence if the medium is to be in static equilibrium there must be an additional stress system whose antisymmetric part is equal and opposite to the antisymmetric part of the Maxwell stress tensor. The previous calculation should include the Maxwell stresses since we have been working to terms second order in the field. The Maxwell stress tensor is bilinear in the electric field and polarization. Since the induced polarization is proportional to the field however, the Maxwell stress tensor is essentially quadratic in the electric field variables. The symmetry of the electrostrictive coefficients Eq. (36) however always leads to symmetric stresses in the medium. This guarantees the rotational invariance of the energy function of the medium. It is therefore apparent that in the calculation just described, Maxwell stresses and local stresses have been lumped together. This will be shown in what follows.

The third order coupling parameter appearing in Eq. (18) can be written as the sum of two terms.

$$D_{\alpha\beta\gamma}^{0mn}(k k' k'') = D_{\alpha\beta\gamma}^N(0 m n k k' k'') + D_{\alpha\beta\gamma}^c(0 m n k k' k'') \quad (37)$$

Superscript N indicates the short range non coulomb contribution to the third order coupling parameter. This term can include the effects of covalency, and general n body interactions. Superscript c refers to two body coulomb interactions and therefore k, k', and k'' must each be equal to one of two types of ions for  $D_{\alpha\beta\gamma}^c(0 m n k k' k'')$  to be non-vanishing. Let us restrict attention to the coulomb term and write the equation of motion Eq. (18) for this term.

$$\begin{aligned} \ddot{v}_\alpha(k|\bar{y}) = & -\frac{1}{2\sqrt{N}} \sum_{\bar{y}, \bar{y}''} \sum_{\substack{\beta \\ n, k', \gamma}} D_{\alpha\beta\gamma}^c(0 m n k k k'') w_{\alpha\beta}(k|\bar{y}') w_{\alpha\gamma}(k''|\bar{y}'') e^{2\pi i \bar{y}'' \cdot \bar{x}(k'' k)} \Delta(\bar{y} + \bar{y}'' - \bar{y}) \\ & -\frac{1}{2\sqrt{N}} \sum_{\bar{y}, \bar{y}''} \sum_{m, k', \beta} D_{\alpha\beta\gamma}^c(0 m o k k' k) w_{\alpha\beta}(k'|\bar{y}') w_{\alpha\gamma}(k|\bar{y}'') e^{2\pi i \bar{y}' \cdot \bar{x}(k' k)} \Delta(\bar{y}' + \bar{y}'' - \bar{y}) + \dots \end{aligned} \quad (38)$$

The two terms appearing in Eq. (38) can be combined if the following relations are used to rewrite the first term.

$$\bar{y}' = \bar{y}''; \beta = \gamma; n \rightarrow m; k'' \rightarrow k'$$

(39)

$$D_{\alpha\beta\gamma}^c \begin{pmatrix} 0 & 0 & n \\ k & k & k'' \end{pmatrix} = D_{\alpha\beta\gamma}^c \begin{pmatrix} 0 & n & 0 \\ k & k'' & k \end{pmatrix}$$

and we obtain

$$\ddot{v}_q(k|\bar{y}) = -\frac{1}{\sqrt{N}} \sum_{\bar{y}, \bar{y}''} \sum_{\gamma} \sum_{m, k', \beta} D_{\alpha\beta\gamma}^c \begin{pmatrix} 0 & m & 0 \\ k & k' & k \end{pmatrix} w_{\alpha\beta}(k'|\bar{y}') w_{\alpha\gamma}(k|\bar{y}'') e^{2\pi i \bar{y}' \cdot \bar{x} \begin{pmatrix} m & 0 \\ k' & k \end{pmatrix}} \Delta(\bar{y}' + \bar{y}'' - \bar{y}) + \dots \quad (40)$$

Using Eq. (13) we can write

$$D_{\alpha\beta\gamma}^c \begin{pmatrix} 0 & m & 0 \\ k & k' & k \end{pmatrix} = \frac{1}{m_k m_{k'}^{\frac{1}{2}}} \phi_{\alpha\beta\gamma}^c \begin{pmatrix} 0 & m & 0 \\ k & k' & k \end{pmatrix} \quad (41)$$

with

$$\phi_{\alpha\beta\gamma}^c \begin{pmatrix} 0 & m & 0 \\ k & k' & k \end{pmatrix} = -q_k q_{k'} \frac{\partial^3}{\partial x_{\alpha} \begin{pmatrix} 0 \\ k \end{pmatrix} \partial x_{\beta} \begin{pmatrix} 0 \\ k' \end{pmatrix} \partial x_{\gamma} \begin{pmatrix} 0 \\ k \end{pmatrix}} \left\{ \frac{1}{|\bar{x} \begin{pmatrix} m \\ k' \end{pmatrix} - \bar{x} \begin{pmatrix} 0 \\ k \end{pmatrix}|} \right\} \quad (42)$$

Since we want to calculate the motion of the center of mass of the unit cell, one must multiply both sides of Eq. (40) by  $m_k^{\frac{1}{2}}$ , sum over  $k$  and then divide by the sum of the masses in the unit cell. We obtain the following equation

$$\ddot{v}_{\alpha\bar{y}} = -\frac{8\pi^2 i}{v_a \sqrt{N}} \sum_k \sum_{\bar{y}, \bar{y}' k, k'} \sum_{\beta, \gamma} \frac{q_k q_{k'}}{\sqrt{m_k m_{k'}}} \frac{y'_{\alpha} y'_{\beta} y'_{\gamma}}{|\bar{y}|^2} w_{\alpha\beta}(k'|\bar{y}') w_{\alpha\gamma}(k|\bar{y}'') \Delta(\bar{y}' + \bar{y}'' - \bar{y}) + \dots \quad (43)$$

after substitution of Eq. (42) into Eq. (40) and the use of

$$\frac{\partial^3}{\partial x_a^{(0)} \partial x_\beta^{(0)} \partial x_\gamma^{(0)}} \sum_m \left[ \frac{2\pi i \bar{y}^i \cdot \bar{x}_{(k')k}^{(m)0}}{|\bar{x}_{(k')k}^{(m)} - \bar{x}_{(k')k}^{(0)}|} \cdot 2\pi i \bar{y}^i \cdot \bar{x}_{(k')k}^{(0)} - \frac{8\pi^2 i}{v_a} \frac{y_a^i y_\beta^j y_\gamma^k}{|\bar{y}|^2} \cdot 2\pi i \bar{y}^i \cdot \bar{x}_{(k')k}^{(0)} \right] \quad (44)$$

The dot over the equality sign in Eq. (44) indicates that we have only exhibited the macroscopic field term on the right hand side of this equation. The inner field term which we neglect, may be grouped with the short range forces. If we perform the sum over  $\beta$ ,  $k'$  and  $k$  in Eq. (43) and let the periodicity volume become infinite we obtain

$$\rho \ddot{v}_{ay} = 2\pi i v_a \sqrt{N} \sum_Y \iint d\bar{y} \, d\bar{y}' E_{a\bar{y}} P_{Y\bar{y}} y_Y^i \delta(\bar{y}' + \bar{y}' - \bar{y}) + \dots \quad (45)$$

This term on the right of Eq. (45) is just the Maxwell stress term that appears in the equation of motion. One can show this in the following way. The elastic equation of motion can be written

$$\rho \ddot{u}_a = \sum_Y \frac{\partial S_{aY}}{\partial X_Y} = \sum_Y P_Y \frac{\partial E_a}{\partial X_Y} + \dots \quad (46)$$

Components of the Maxwell stress tensor are given by

$$S_{aY}^M = E_a P_Y \quad (47)$$

Using the following Fourier decomposition of electric field and polarisation

$$E_a = v_a \sqrt{N} \int_{-\infty}^{\infty} E_{a\bar{y}} e^{2\pi i \bar{y} \cdot \bar{r}} d\bar{y}; P_Y = v_a \sqrt{N} \int_{-\infty}^{\infty} P_{Y\bar{y}} e^{2\pi i \bar{y} \cdot \bar{r}} d\bar{y} \quad (48)$$

it can be shown that the Maxwell stress term exhibited explicitly in Eq. (46) is identical with the term in Eq. (45). Hence we have shown that the microscopic lattice equations of motion that have been used to obtain expressions for the electrostrictive constants, contain the Maxwell stress terms.

### 4.3 Electrostriction of Ferroelectric Materials

The piezoelectric and electrostrictive behavior of ferroelectric materials has been treated extensively in the past<sup>10</sup>. Many of the measurements have been made on materials in the polarized phase. In this phase the materials are piezoelectric exhibiting a linear relation between stress and applied field. The interpretation of measurements in the polarized phase is complicated by the presence of ferroelectric domains. In the unpolarized or cubic phase the material is electrostrictive, i. e., there is a quadratic dependence of the stress on electric field. Devonshire's<sup>4</sup> treatment of the electromechanical properties of  $\text{BaTiO}_3$  assumes that the piezoelectric coefficients in the polarized phase are related simply to the electrostrictive coefficients in the unpolarized phase. Verification of Devonshire's theory has formed the basis for much of the work on electrostriction. To the extent that the Devonshire theory is valid, the theory presented in this paper should form a basis for understanding the microscopic origin of the piezoelectric and electrostrictive behavior of  $\text{BaTiO}_3$  and related isomorphs. In any event, the microscopic theory presented in Section 4.2 should be valid for application in the unpolarized phase of these materials.

Measurements on single crystal barium titanate<sup>11</sup> and strontium titanate<sup>12</sup> have been made above the Curie temperature as a function of temperature. Over the range of measurement, these materials are paraelectric having a large dielectric constant which obeys a Curie-Weiss law. The measured temperature variation of the electrostrictive coefficients  $d$ , is given by

$$d \sim \frac{1}{(T - T_c)^2} \quad (49)$$

$T_c$  is the Curie temperature obtained from high temperature dielectric measurements. This temperature variation is in agreement with the result predicted from Devonshire's phenomenological theory. That this temperature variation also results from the microscopic expressions obtained is shown in the following way.

The frequency of the low lying "ferroelectric" mode of  $\text{SrTiO}_3$  has an observed temperature dependence given by<sup>13</sup>

$$\omega \left( \frac{0}{F} \right) \sim (T - T_c)^{1/2} \quad (50)$$

Such a temperature dependent mode should also be present in  $\text{BaTiO}_3$  and its isomorphs<sup>6, 14</sup>. This is the mode which dominates the low frequency dielectric behavior. This mode should also dominate the electrostrictive behavior due to its relatively low frequency and large oscillator strength<sup>15</sup>. Therefore, in the expression for the electrostrictive coefficients, Eq. (35), contributions are neglected from all optical modes other than the soft ferroelectric mode. The result can be written

$$d_{\alpha\nu, \delta\Delta} = \frac{1}{v_a} \sum_{\substack{mk^m\beta \\ nk^n\gamma \\ k}} \sum_{\substack{k^m \\ k^n}} D_{\alpha\beta\gamma}(\text{omn})_{kk'k''} \frac{\epsilon_{\delta}^*(k^m | \frac{0}{F}) \epsilon_{\beta}(k' | \frac{0}{F}) \epsilon_{\Delta}^*(k^n | \frac{0}{F}) \epsilon_{\gamma}(k'' | \frac{0}{F})}{\omega^4(\frac{0}{F})} \\ \times \sqrt{\frac{m_k}{m_{k^m} m_{k^n}}} q_{k^m} q_{k^n} X_{\nu}(\text{om})_{kk'} \sim \frac{1}{(T - T_c)^2} \quad (51)$$

The temperature dependence of the soft mode frequency (Eq. 50) therefore leads to the observed temperature dependence of the electrostrictive coefficients.

Since we have the electrostrictive coefficients in terms of the microscopic parameters of the lattice, let us see whether these parameters can be reasonably chosen to reproduce the measured value. The room temperature value of  $d_{11, 11}$  for  $\text{SrTiO}_3$  as reported by Winter and Rupprecht<sup>13</sup> will be calculated. This value is

$$d_{11, 11} = 9.53 \times 10^{-7} \frac{\text{Newton}}{(\text{Volt})^2} \quad (52)$$

This coefficient is written

$$d_{11', 11} = \frac{1}{v_a} \sum_{\substack{m, k' \\ n, k'' \\ k}} \sum_{k'''} D_{111} \left( \begin{smallmatrix} o & m & n \\ k & k' & k'' \end{smallmatrix} \right) \frac{\epsilon(k''') \epsilon(k') \epsilon(k'') \epsilon(k'')}{\omega^4 \left( \begin{smallmatrix} o \\ F \end{smallmatrix} \right)}$$

$$\frac{1}{\sqrt{m}} q_{k'''} q_{k''} X \left( \begin{smallmatrix} o & m \\ k & k' \end{smallmatrix} \right) \quad (53)$$

This expression can be evaluated simply with use of the linear chain model of a ferroelectric.<sup>16</sup> For the chain model, we have

$$\epsilon(1) = - \frac{1}{\sqrt{2}} \quad ; \quad q_1 = - ne/b$$

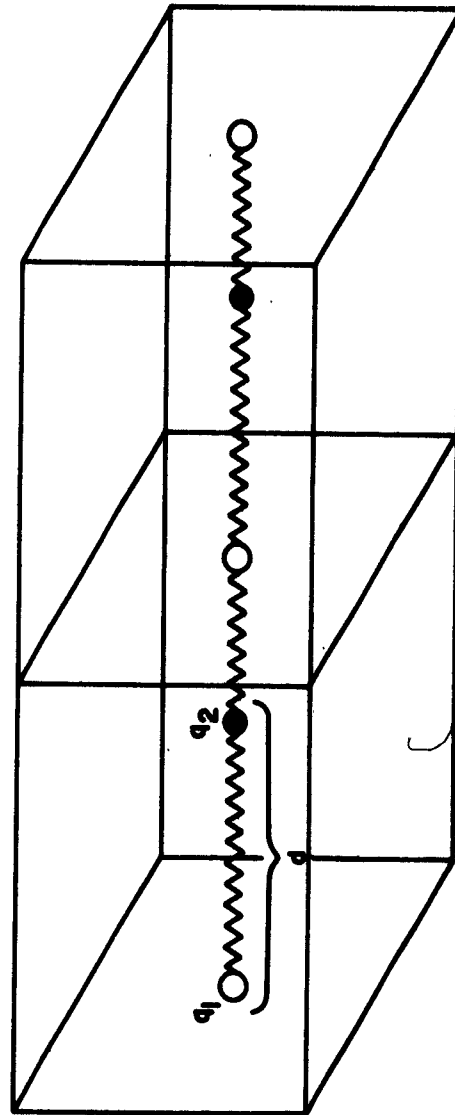
$$\epsilon(2) = \frac{1}{\sqrt{2}} \quad ; \quad q_2 = ne/b$$
(54)

$n$  is the number of electronic charges on the ions.  $e$  is the electronic charge.  $b$  is a constant which includes effects of electronic polarizability and makes the  $q_1$  and  $q_2$  essentially, effective charges. Two unit cells of the chain model are shown in Figure 1. After the sums have been performed in Eq. (53) we obtain the relatively simple expression for  $d_{11', 11}$ .

$$d_{11', 11} = \frac{4a (ne/b)^2 d}{m^2 \omega^4 \left( \begin{smallmatrix} o \\ F \end{smallmatrix} \right) v_a} \quad (55)$$

$a$  is a third order coupling coefficient.  $d$  is a lattice parameter shown in Figure 1

Values have been substituted for all of these quantities (except  $n$ ) in a manner discussed previously. The value of  $n$  was then adjusted so that the value of (55) was equal to the observed value (52). In this fashion one obtains the reasonable value of  $n = 2$  electronic charges which is further substantiation for the treatment presented.



○ Oxygen  
● Titanium

FIGURE 1



#### 4.4 Appendix

In this section we sketch how the symmetry relations (Eq. 36) are obtained. The symmetry of the electrostrictive coefficient (Eq. 35) upon the following interchange

$$\delta \rightleftharpoons \Delta \quad (56)$$

is obtained simply by noting the following interchanges

$$k^m = k^n ; k' = k'' ; \beta = \gamma ; j' = j'' ; m = n \quad (57)$$

and by using the translational invariance condition (Eq. 25).

The symmetry of the electrostrictive coefficient upon the interchange

$$a \rightleftharpoons v \quad (58)$$

is somewhat more involved. Upon interchange of  $a$  and  $v$  in equation (35) we obtain

$$d_{va, \delta\Delta} = \frac{1}{2v_a} \sum_{j', j''} \sum_{\substack{mk'\beta \\ nk''\gamma \\ k}} \sum_{\substack{k^m \\ k^n}} D_{v\beta\gamma} \left( \begin{smallmatrix} o & m & n \\ k & k' & k'' \end{smallmatrix} \right) \frac{\epsilon_{\delta}^*(k^m | j') \epsilon_{\beta}(k' | j') \epsilon_{\Delta}^*(k^n | j'') \epsilon_{\gamma}(k'' | j'')}{\omega^2(j')} \frac{\epsilon_{\Delta}^*(k^n | j'') \epsilon_{\gamma}(k'' | j'')}{\omega^2(j'')} \\ \times \sqrt{\frac{m_k}{m_{k^m} m_{k^n}}} q_{k^m} q_{k^n} X_a \left( \begin{smallmatrix} o & m \\ k & k' \end{smallmatrix} \right) \quad (59)$$

The rotational invariance condition connecting third order and second order coupling parameters can be written<sup>17</sup>.

$$\sum_{m, k} \phi_{v\beta\gamma} \left( \begin{smallmatrix} o & m & n \\ k & k' & k'' \end{smallmatrix} \right) X_a \left( \begin{smallmatrix} o & m \\ k & k' \end{smallmatrix} \right) + \phi_{v\gamma} \left( \begin{smallmatrix} o & n \\ k' & k'' \end{smallmatrix} \right) \delta_{\beta a} + \phi_{\beta v} \left( \begin{smallmatrix} o & n \\ k' & k'' \end{smallmatrix} \right) \delta_{\gamma a} \\ = \sum_{m, k} \phi_{a\beta\gamma} \left( \begin{smallmatrix} o & m & n \\ k & k' & k'' \end{smallmatrix} \right) X_v \left( \begin{smallmatrix} o & m \\ k & k' \end{smallmatrix} \right) + \phi_{a\gamma} \left( \begin{smallmatrix} o & n \\ k' & k'' \end{smallmatrix} \right) \delta_{\beta v} + \phi_{\beta a} \left( \begin{smallmatrix} o & n \\ k' & k'' \end{smallmatrix} \right) \delta_{\gamma v} \quad (60)$$

Using equations (35), (59), and (60), and the defining equations (12) and (13), one can write

$$d_{\nu\alpha, \delta\Delta} - d_{\alpha\nu, \delta\Delta} = \frac{1}{2v_a} \sum_{j, j'} \sum_{k', \beta} \sum_{k''} \{ D_{\alpha\gamma}(\overset{on}{k'k''}) \delta_{\beta\nu} + D_{\beta\alpha}(\overset{on}{k'k''}) \delta_{\gamma\nu} - D_{\nu\gamma}(\overset{on}{k'k''}) \delta_{\beta\alpha} - D_{\beta\nu}(\overset{on}{k'k''}) \delta_{\gamma\alpha} \} \times \frac{q_{k''} q_{k'}}{m_{k''} m_{k'}} \frac{\epsilon_{\delta}^*(k'' | \overset{o}{y},) \epsilon_{\beta}(k' | \overset{o}{j},)}{\omega_{j,}^2(\overset{o}{j},)} \frac{\epsilon_{\Delta}^*(k'' | \overset{o}{j},) \epsilon_{\gamma}(k' | \overset{o}{j},)}{\omega_{j,}^2(\overset{o}{j},)} \quad (61)$$

If the contribution to the macroscopic field is separated from the contributions linear field and noncoulomb forces in the second order coupling parameter.

$$\phi_{\gamma u}(\overset{l}{k} k') = 4\pi q_k q_{k'} \frac{y_{\gamma} y_u}{|\bar{y}|^2} + \phi'_{\gamma u}(\overset{l}{k} k') \quad (62)$$

or

$$D_{\gamma u}(\overset{l}{k} k') = 4\pi \frac{q_k q_{k'}}{\sqrt{m_k m_{k'}}} \frac{y_{\gamma} y_u}{|\bar{y}|^2} + D'_{\gamma u}(\overset{l}{k} k') \quad (63)$$

It can be shown that the term on the right of equation (61) vanishes thereby proving the validity of equation (36).

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## 5. OPTICAL VIBRATIONS IN PEROVSKITE MATERIALS

It is now generally agreed that the interesting paraelectric properties of the perovskites result from the temperature dependence of a low lying transverse optical mode. Indeed, one can understand qualitatively the origin of the Curie-Weiss behavior of the dielectric constant, nonlinear response, electromechanical behavior, and microwave loss mechanisms in terms of a general lattice dynamical approach. A more detailed and quantitative understanding of these and other phenomena is frustrated, however, by our lack of knowledge concerning the actual ionic motions associated with the soft ferroelectric mode and other optical modes of the material. There have been various attempts to interpret optical data and assign motions to the optically active vibrations; however, none of the work to date is conclusive. In this we briefly describe an approach to this problem which has yielded results of some interest.

The perovskite structure has five atoms in the unit cell and therefore a total of fifteen branches in its spectrum. Three of these are of the acoustic type. Three of these are of a torsional type and optically inactive. Of the nine remaining, six are transverse (doubly degenerate) optically active vibrations and three are optically inactive longitudinal vibrations. The long wavelength optically active modes can be characterized by the relative motions of the five inequivalent sublattices. Due to the cubic symmetry of the structure and the fact that three of the sublattices are composed of oxygen atoms it is easily seen that if one restricts attention to vibrations along one of the cartesian axes, there are in general seven sublattice couplings. Since there are three observed optical frequencies ( $\text{SrTiO}_3$ ),<sup>1</sup> one can choose three of the sublattice couplings different from zero and have a completely specified problem. One can then solve for the sublattice couplings and also for the relative motion of the sublattices for each mode. This calculation has been carried out for the sublattices as labelled in Fig. 2, and for the following couplings:

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<sup>1</sup>W. G. Spitzer, R. C. Miller, D. A. Kleinman and L. E. Howarth, Phys. Rev. 126, 1710 (1962).

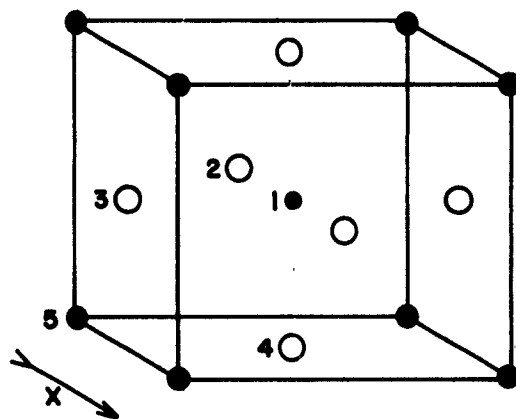


FIGURE 2

- $k_1$ :  $O_2$  - Ti coupling  
 $k_2$ :  $O_2$  -  $O_3$  and  $O_2$  -  $O_4$  coupling  
 $k_3$ :  $Sr$  -  $O_3$  and  $Sr$  -  $O_4$  coupling

The equations of motion are

$$\begin{aligned}
 m_1 \ddot{x}_1 &= -2k_1 x_1 + 2k_1 x_2 \\
 m_2 \ddot{x}_2 &= -2k_1 x_2 + 2k_1 x_1 - 8k_2 x_2 + 4k_2 x_3 + 4k_2 x_4 \\
 m_3 \ddot{x}_3 &= -4k_3 x_3 + 4k_3 x_5 - 4k_2 x_3 + 4k_2 x_2 \\
 m_4 \ddot{x}_4 &= -4k_3 x_4 + 4k_3 x_5 - 4k_2 x_4 + 4k_2 x_2 \\
 m_5 \ddot{x}_5 &= -8k_3 x_5 + 4k_3 x_3 + 4k_3 x_4
 \end{aligned}$$

The solutions of these equations are presently being analyzed; however, one interesting feature that automatically comes out of the calculation is the following. The high frequency mode is a vibration of the  $O_2$  sublattice against the  $O_3$  and  $O_4$  sublattices which are rigidly fixed. The two lower frequency motions essentially involve a fairly rigid motion of the entire oxygen framework ( $O_2$ ,  $O_3$ , and  $O_4$  sublattices). This is consistent with the observed ionic displacements from the cubic phase of ferroelectric materials of the perovskite structure as the material becomes polarized.<sup>2</sup> The oxygen framework remains relatively rigid. Since this indicates that oxygen-oxygen couplings are relatively strong it is therefore reasonable that the highest frequency mode is a vibration between the oxygen sublattices. Since the two other modes involve little relative motion of the oxygen

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<sup>2</sup>G. Shirane, R. Pepinsky, and B. C. Frazer, Phys. Rev. 97, 1179 (1955);  
 B. C. Frazer, H. Donner, R. Pepinsky, Phys. Rev. 100, 745 (1955);  
 H. T. Evans, Mass. Inst. Technol. Lab. Insulation Research Tech. Rept.  
 No. 58 (1953).

sublattices, it is again reasonable that their frequencies are both relatively distant from the highest frequency as has been observed. That this high frequency is a common feature of the perovskite structure can be seen by the reflectivity spectra illustrated in Fig. 3.<sup>3</sup> through 16.

Similar calculations have been performed for a four sublattice model in which bond angle couplings have been introduced between the titanium and O<sub>3</sub> and O<sub>4</sub> oxygen atoms. The observed torsional infrared inactive frequency was used to completely determine the four couplings.<sup>4</sup> Again similar results were obtained for the high frequency mode.

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<sup>3</sup>The reflectivity data presented in Fig. 3 has been obtained by G. Rupprecht prior to his leaving Raytheon Company.

<sup>4</sup>We are indebted to R. A. Cowley for giving us the value of this infrared inactive frequency which he obtained from inelastic neutron scattering measurements. See Phys. Rev. Letters 9, 159 (1962).



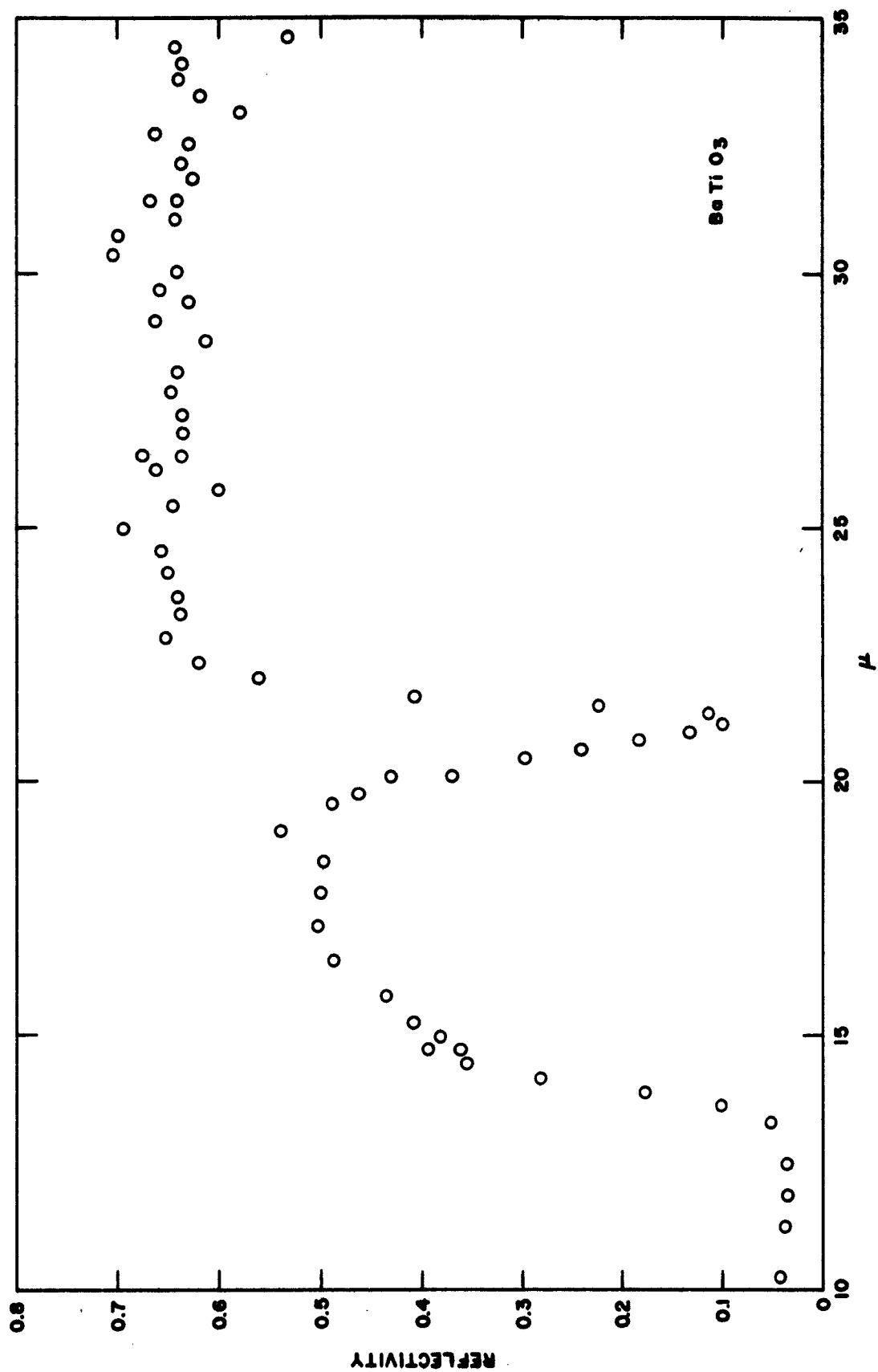


FIGURE 3

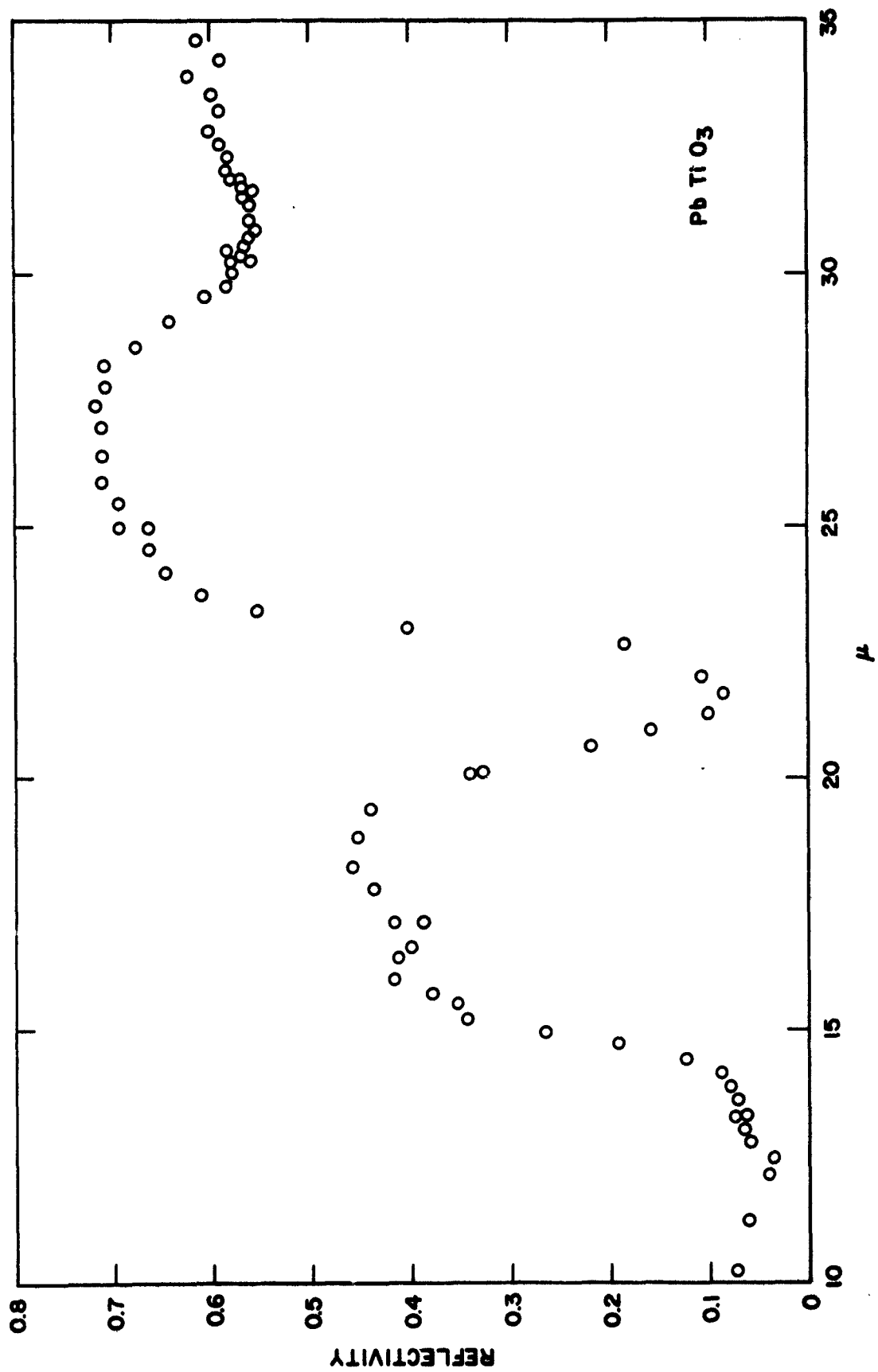


FIGURE 4

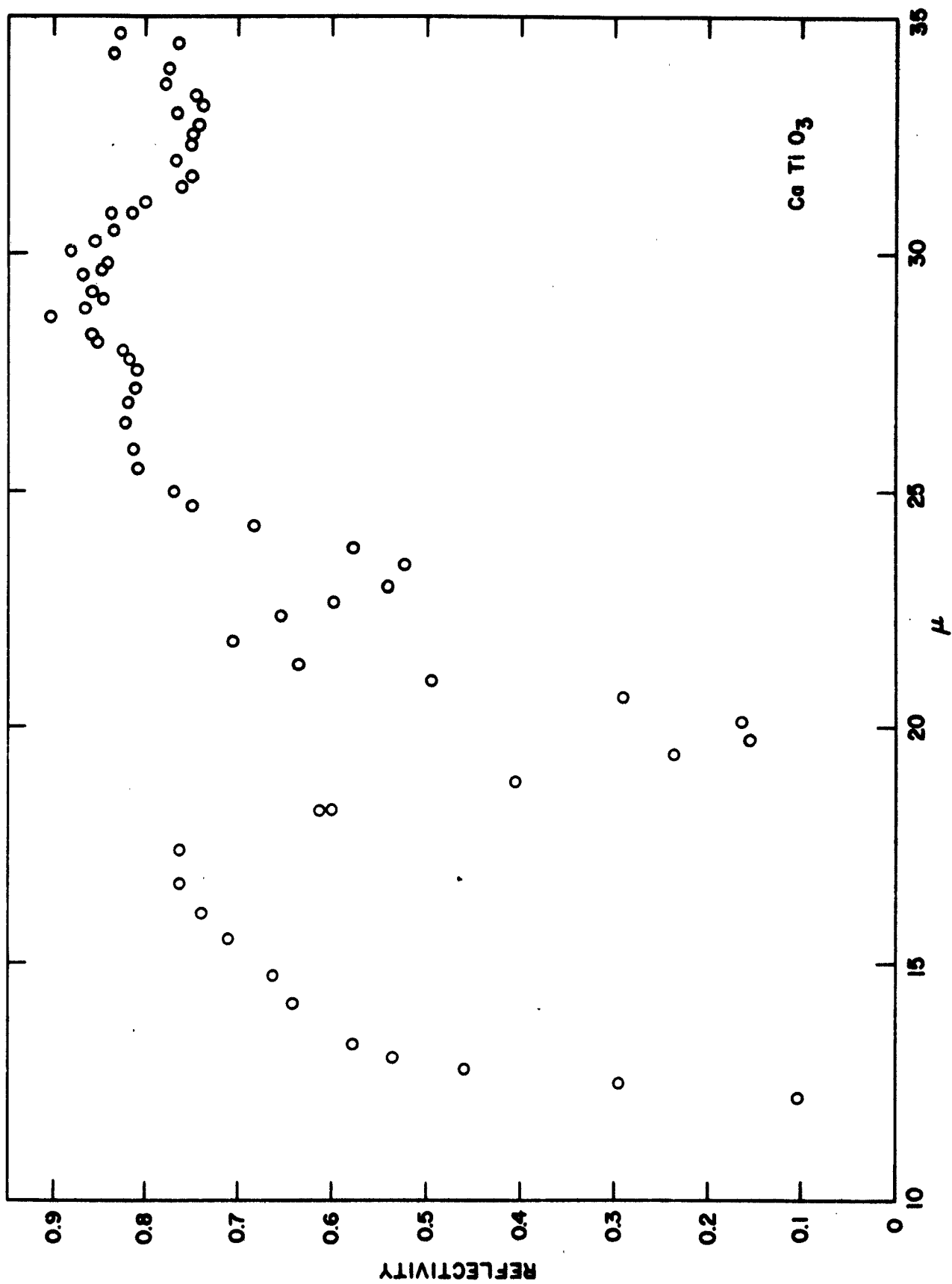


FIGURE 5

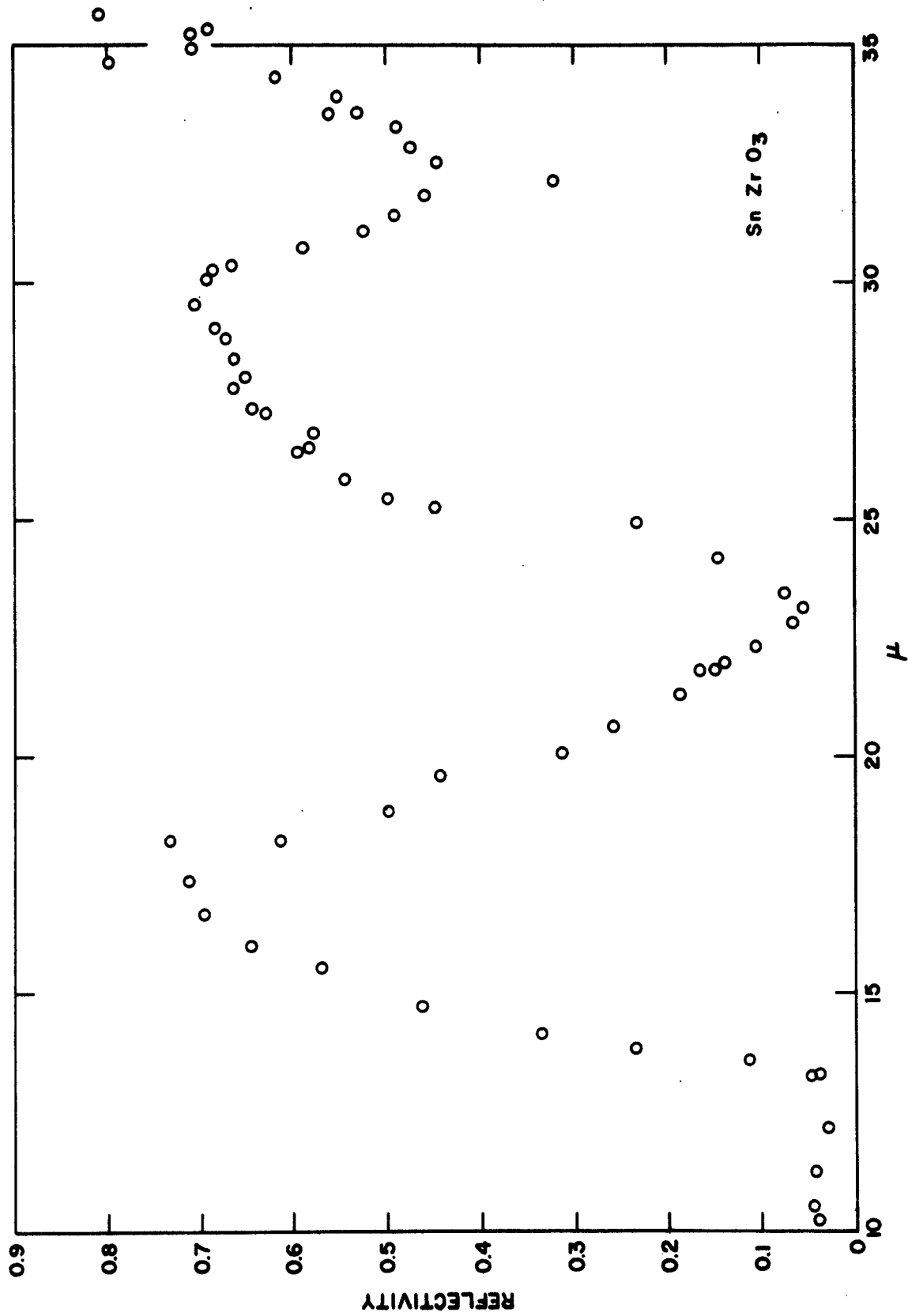


FIGURE 6

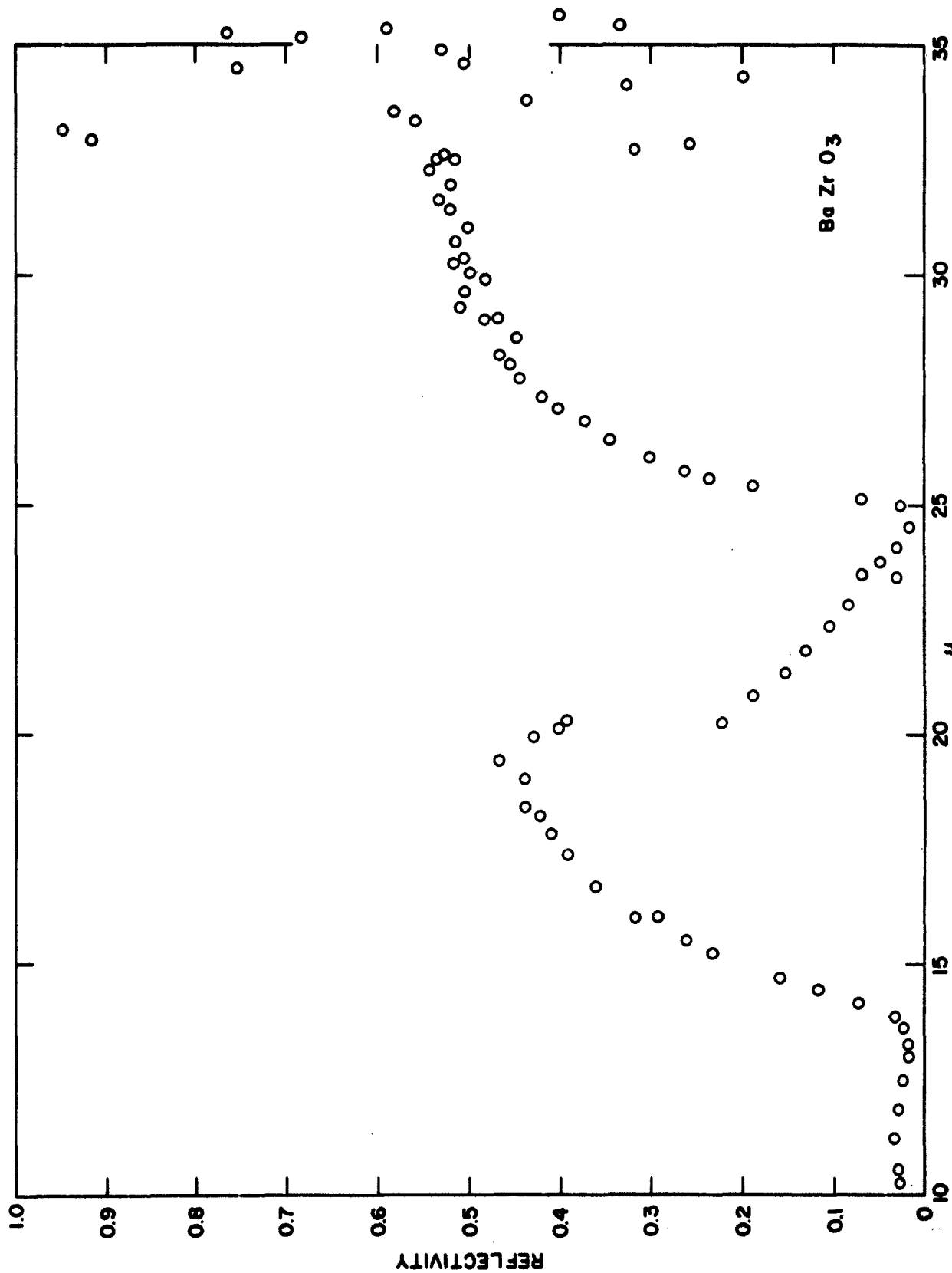


FIGURE 7

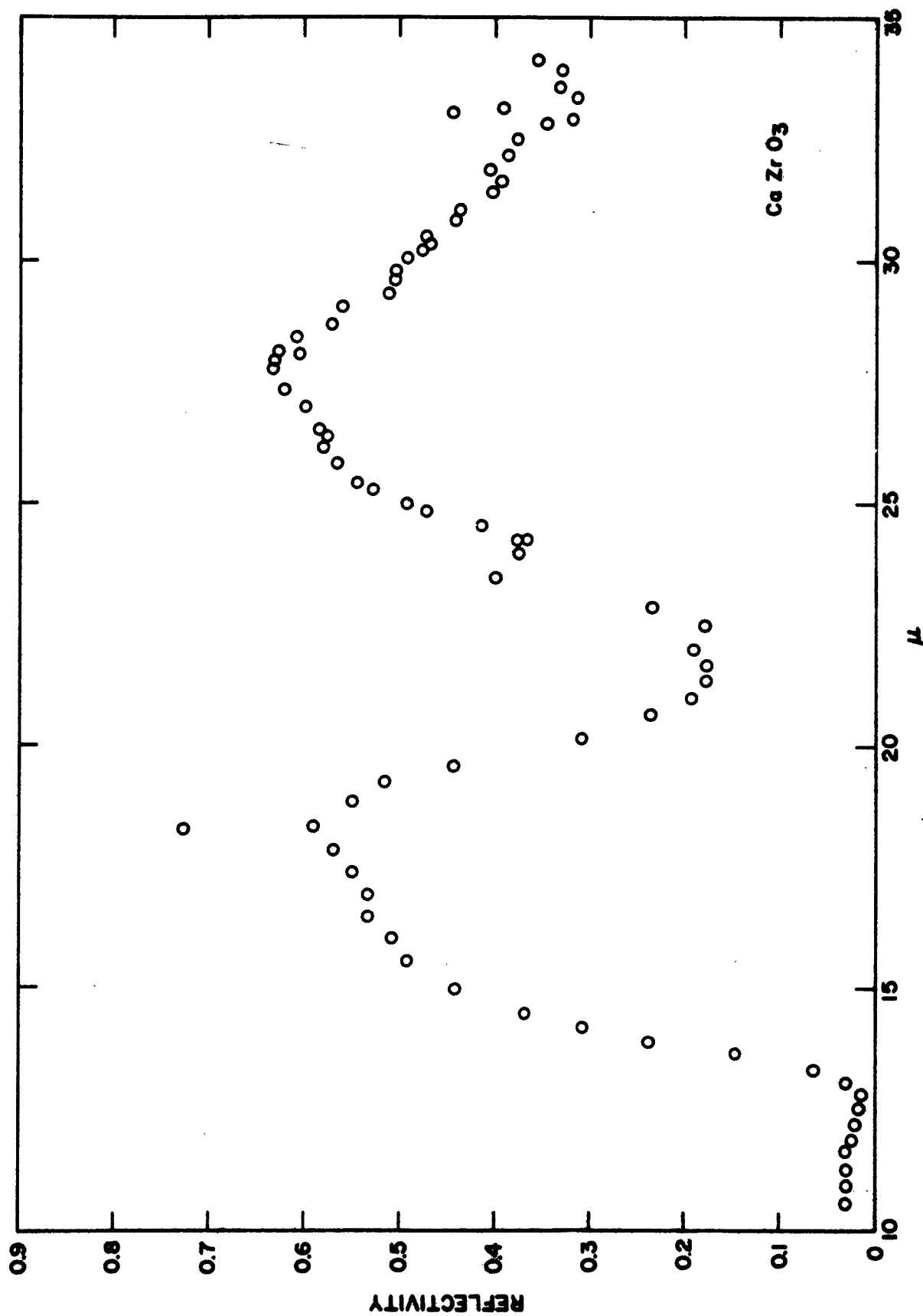


FIGURE 8

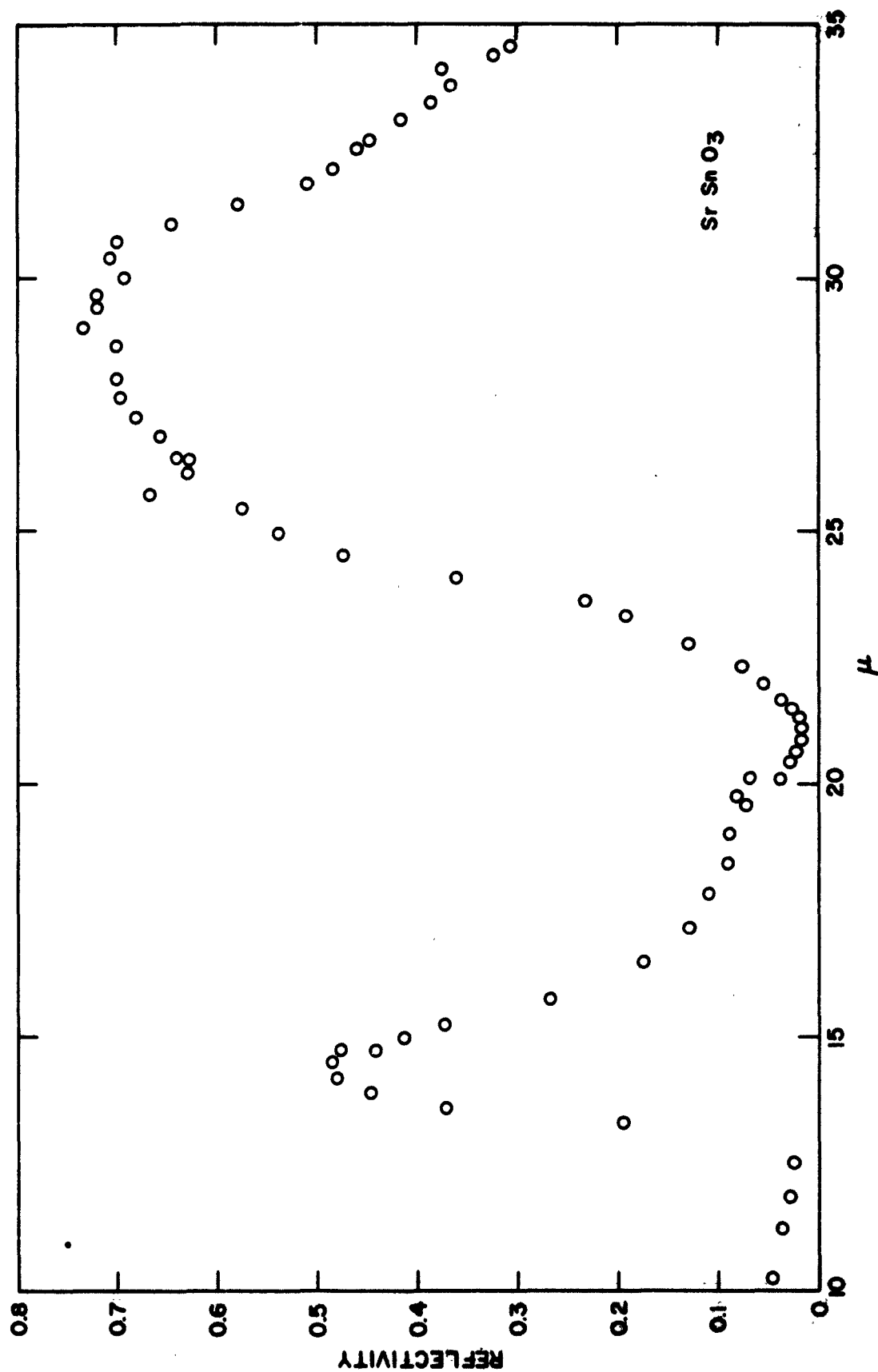


FIGURE 9

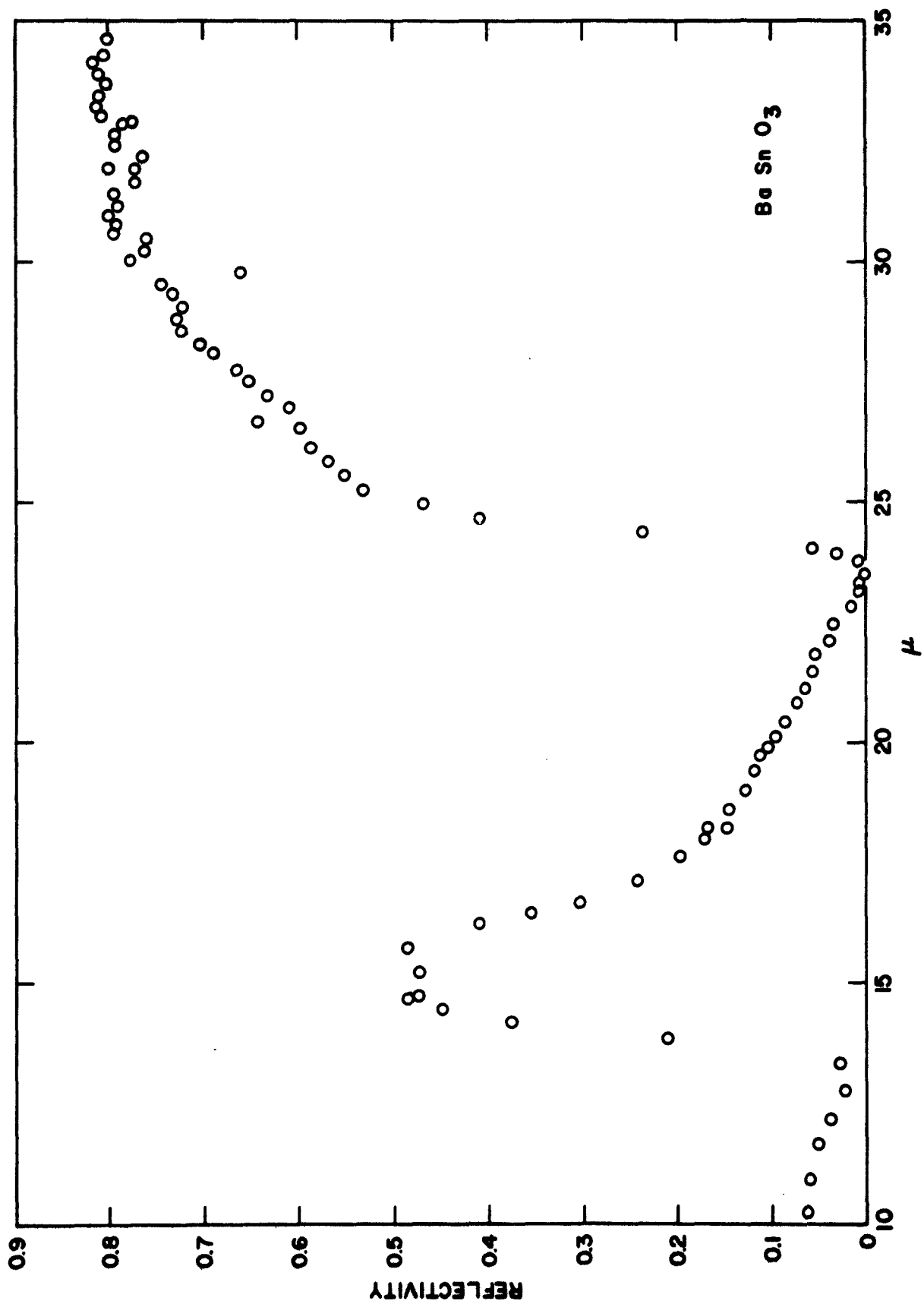


FIGURE 10



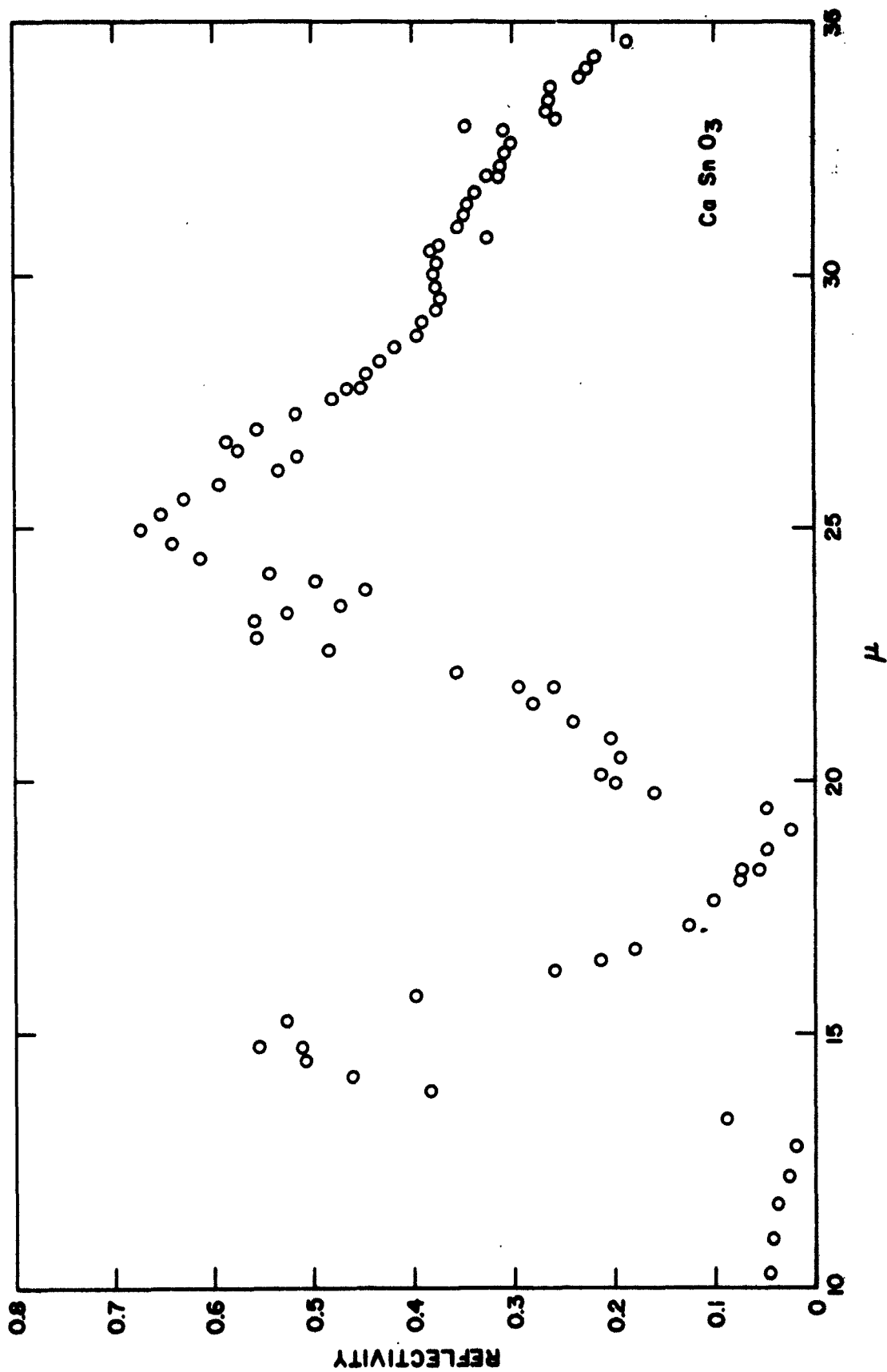


FIGURE 11

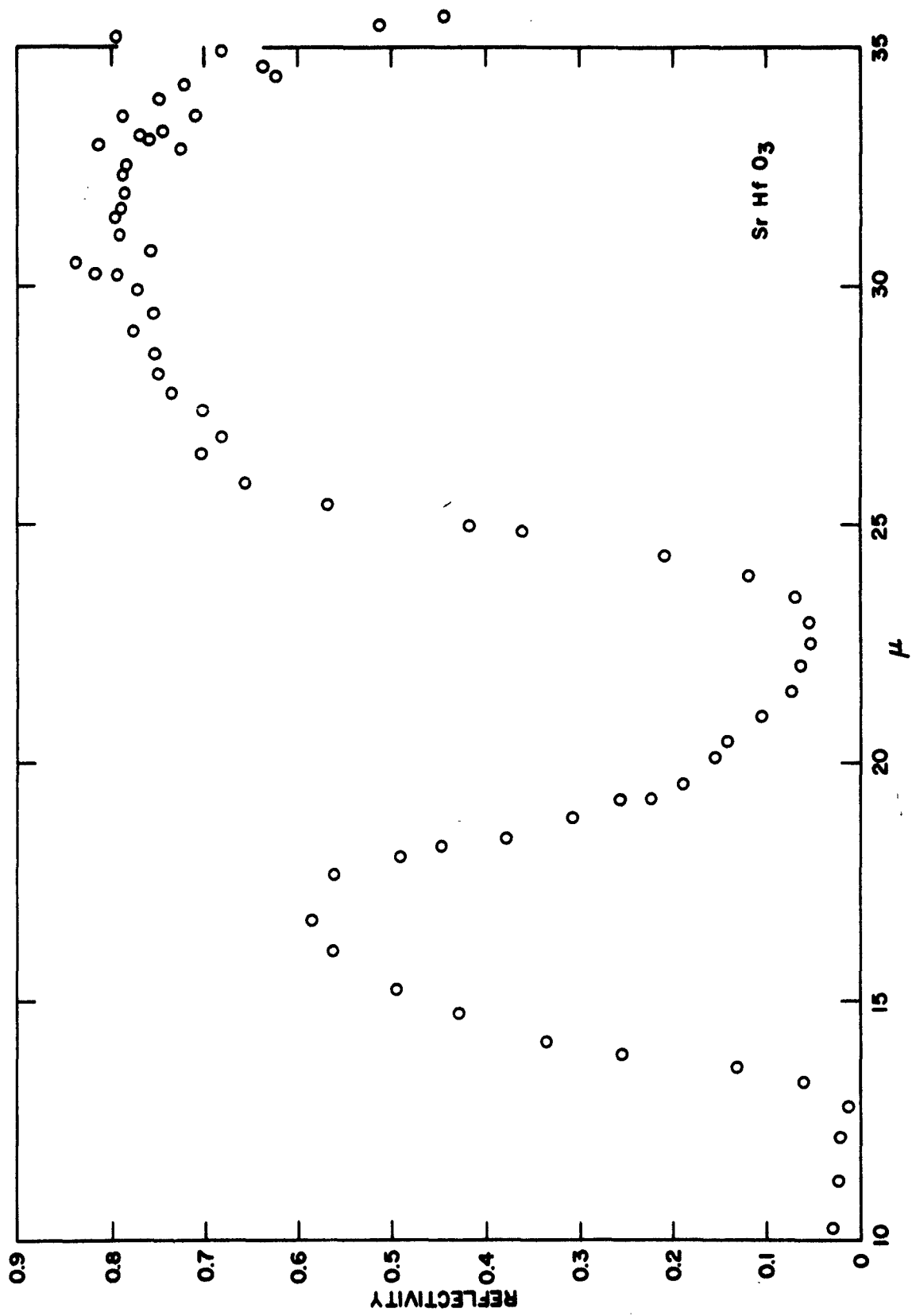


FIGURE 12

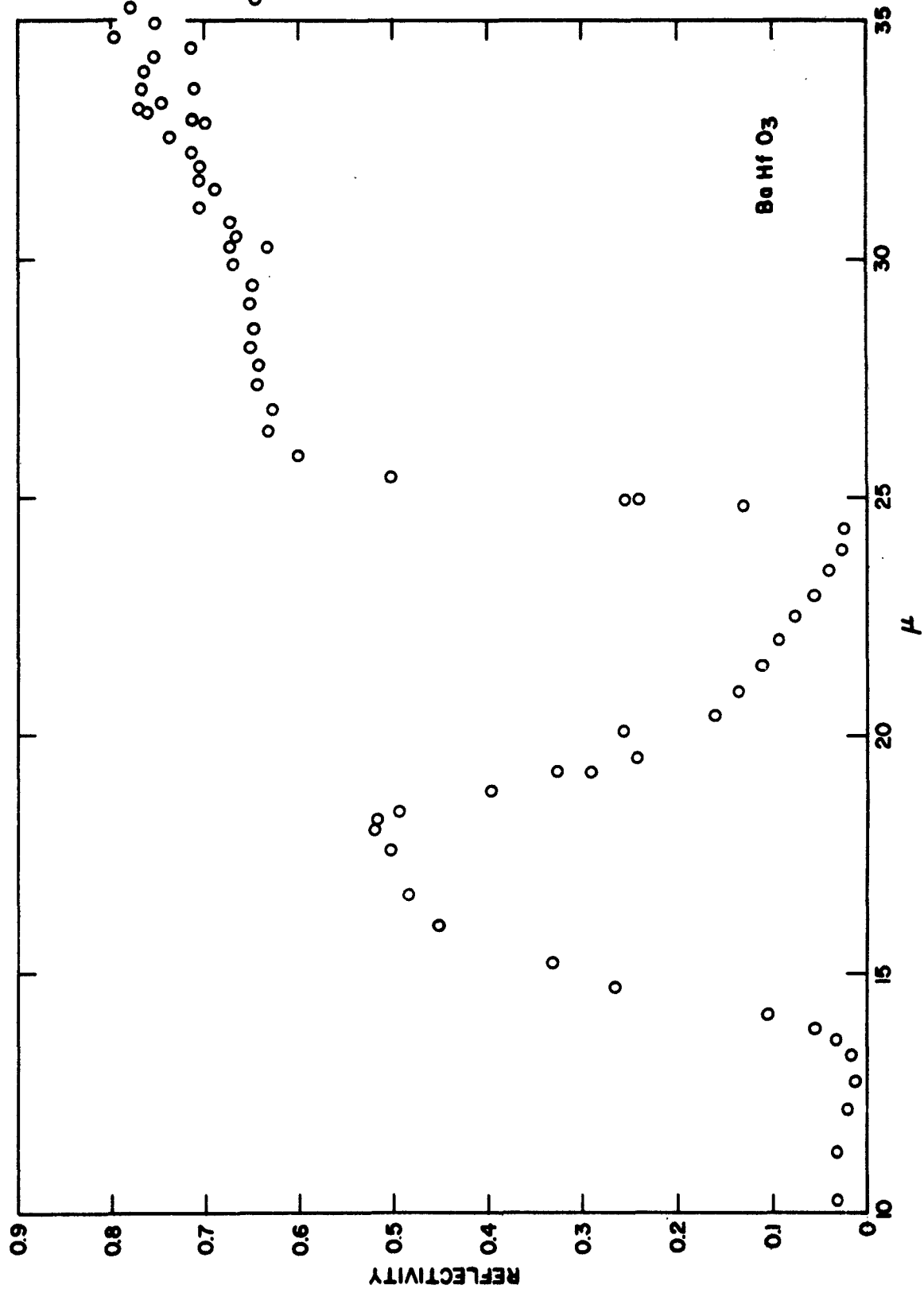


FIGURE 13

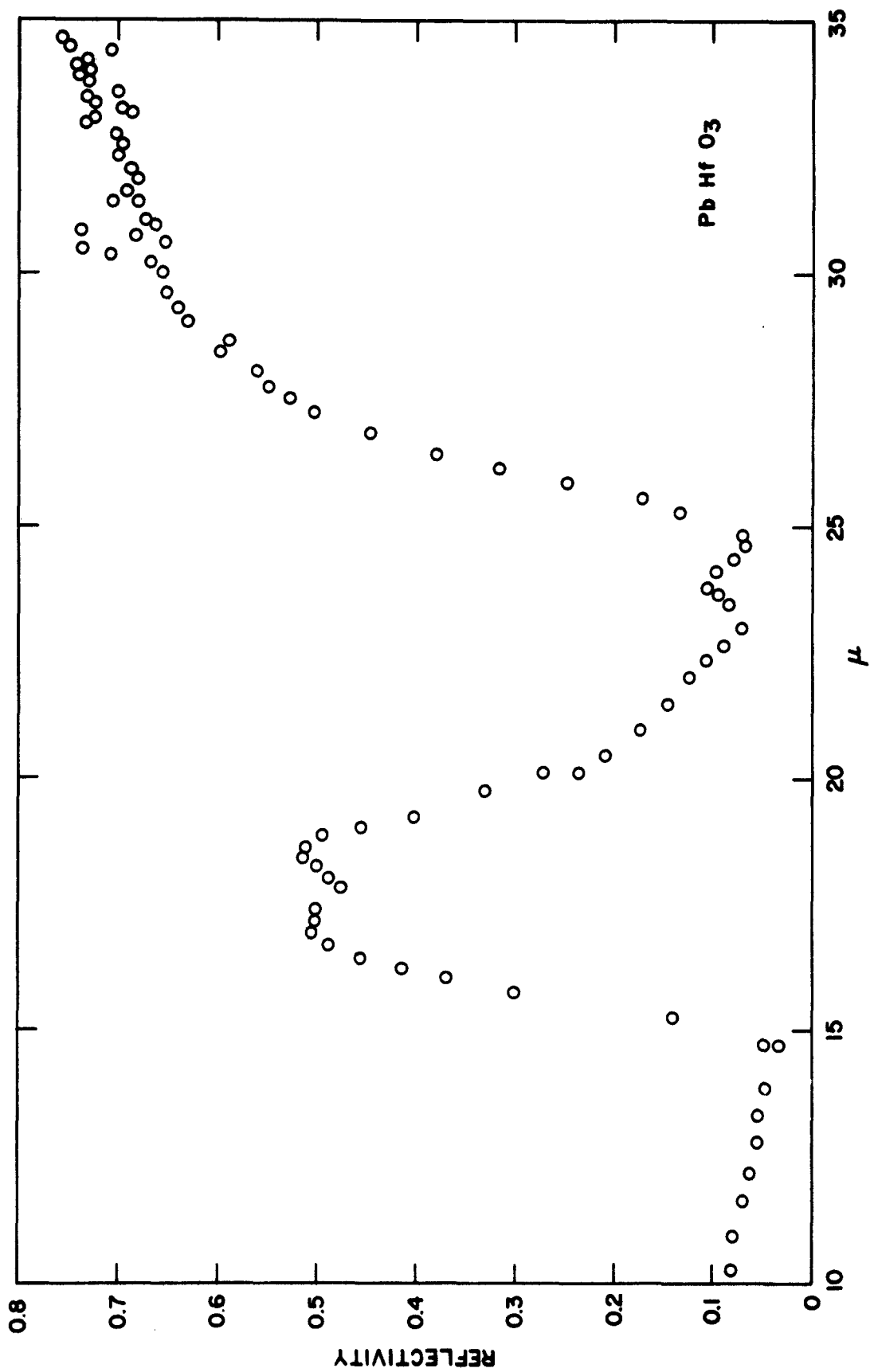


FIGURE 14

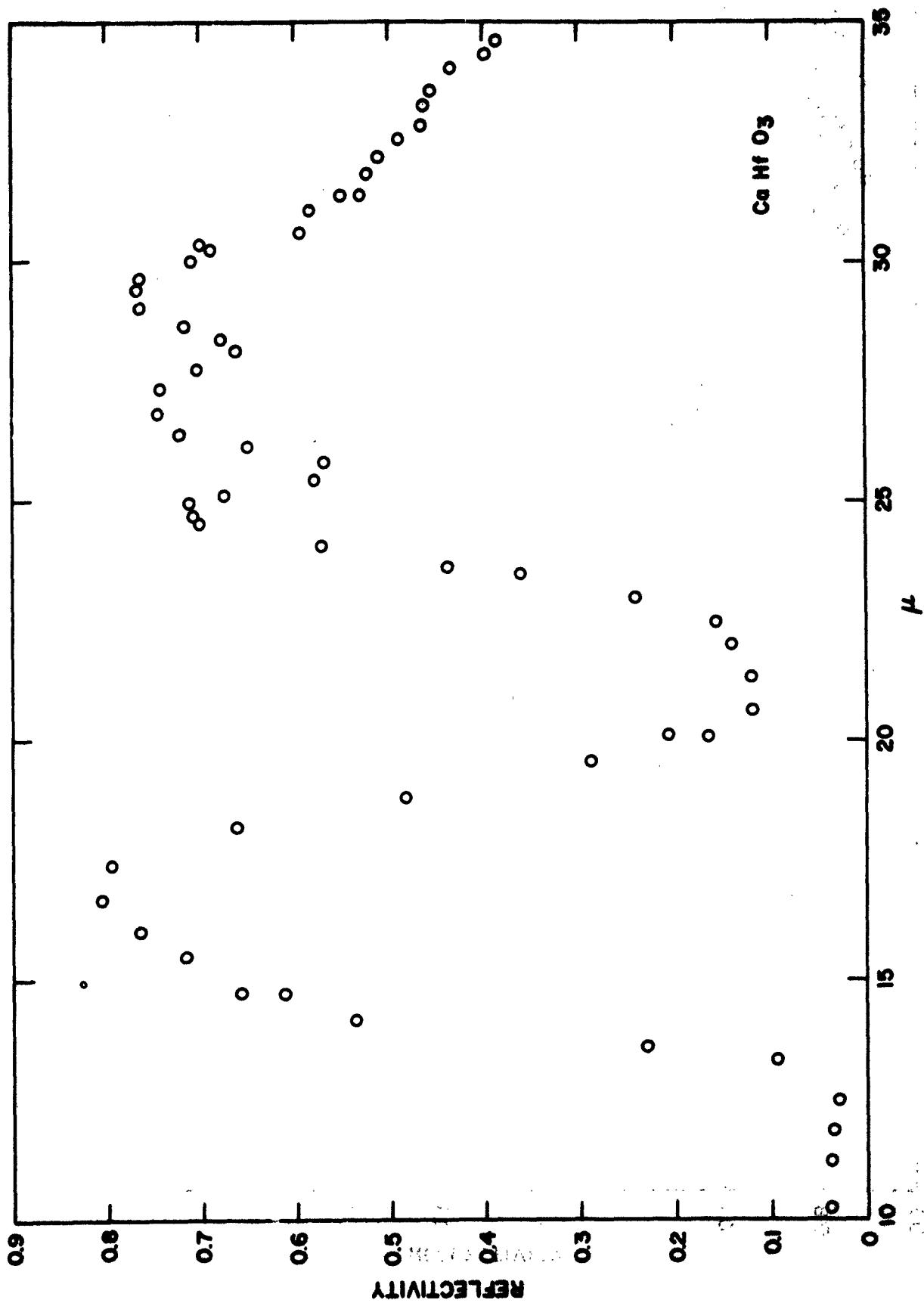


FIGURE 15

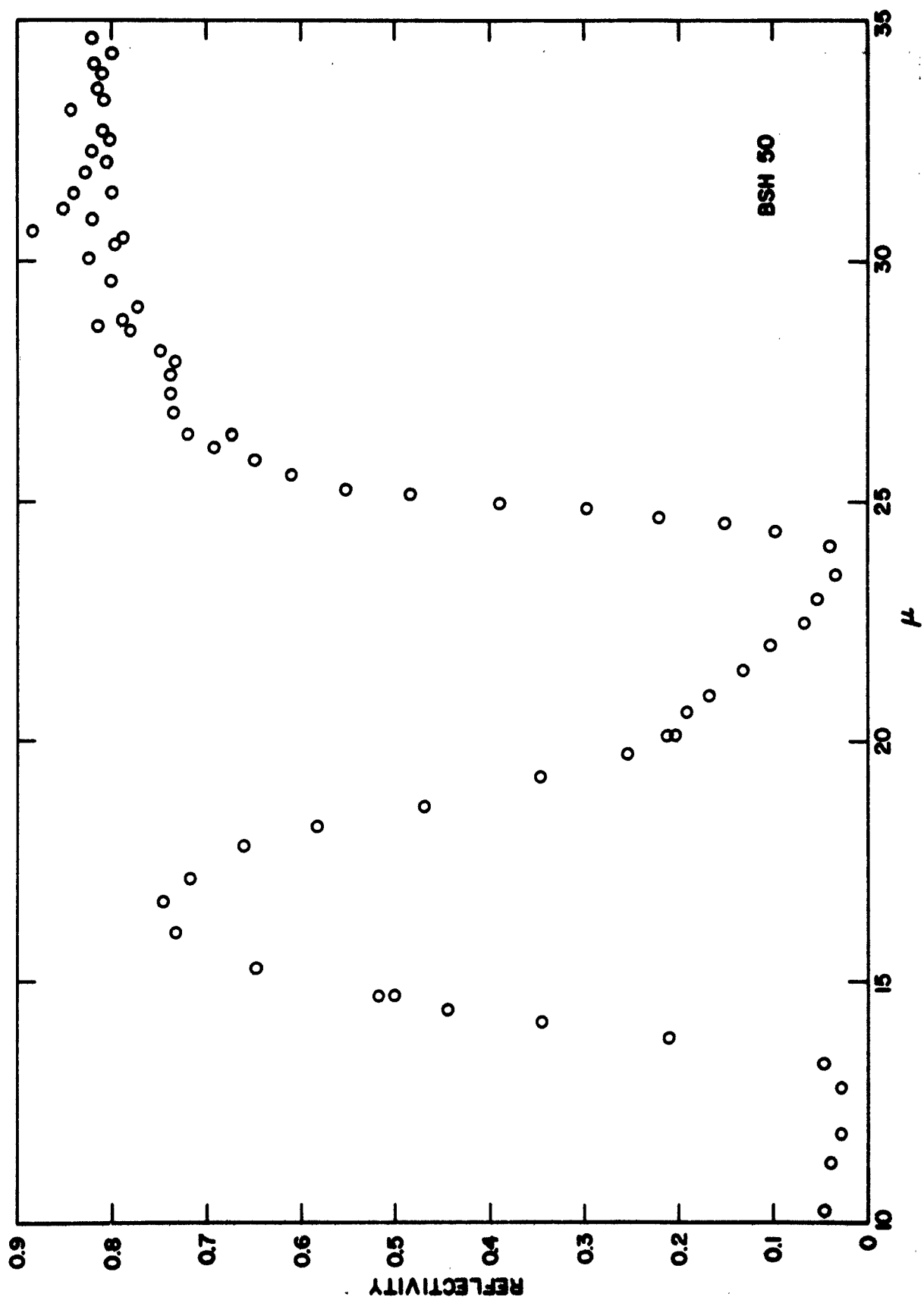


FIGURE 16

## 6. ELASTIC CONSTANTS OF $\text{KTaO}_3$

The elastic stiffness constant,  $C_{11}$ , of  $\text{KTaO}_3$  was measured as a function of temperature in order to determine whether  $\text{KTaO}_3$  exhibits a phase transformation similar to that observed in  $\text{SrTiO}_3$  at 110°K. Since the microwave losses increase rapidly at such a transformation its presence might seriously limit the device applications of a material.

The elastic constant was determined by measuring the velocity of propagation of a longitudinal ultrasonic pulse along a [100] crystallographic axis of a single crystal since  $v_{\text{long.}} = \sqrt{C_{11}/\rho}$ . The apparatus and the techniques used are identical to those described by Bell and Rupprecht for  $\text{SrTiO}_3$ <sup>1</sup> so they will not be discussed here. Measurements have been made from room temperature to liquid nitrogen and no transition has been observed in this range. The results are shown in Fig. 17. A change in ultrasonic attenuation which was observed was not reproduced in other samples.

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<sup>1</sup>R. O. Bell and G. Rupprecht, Phys. Rev. 129, 90 (1963).

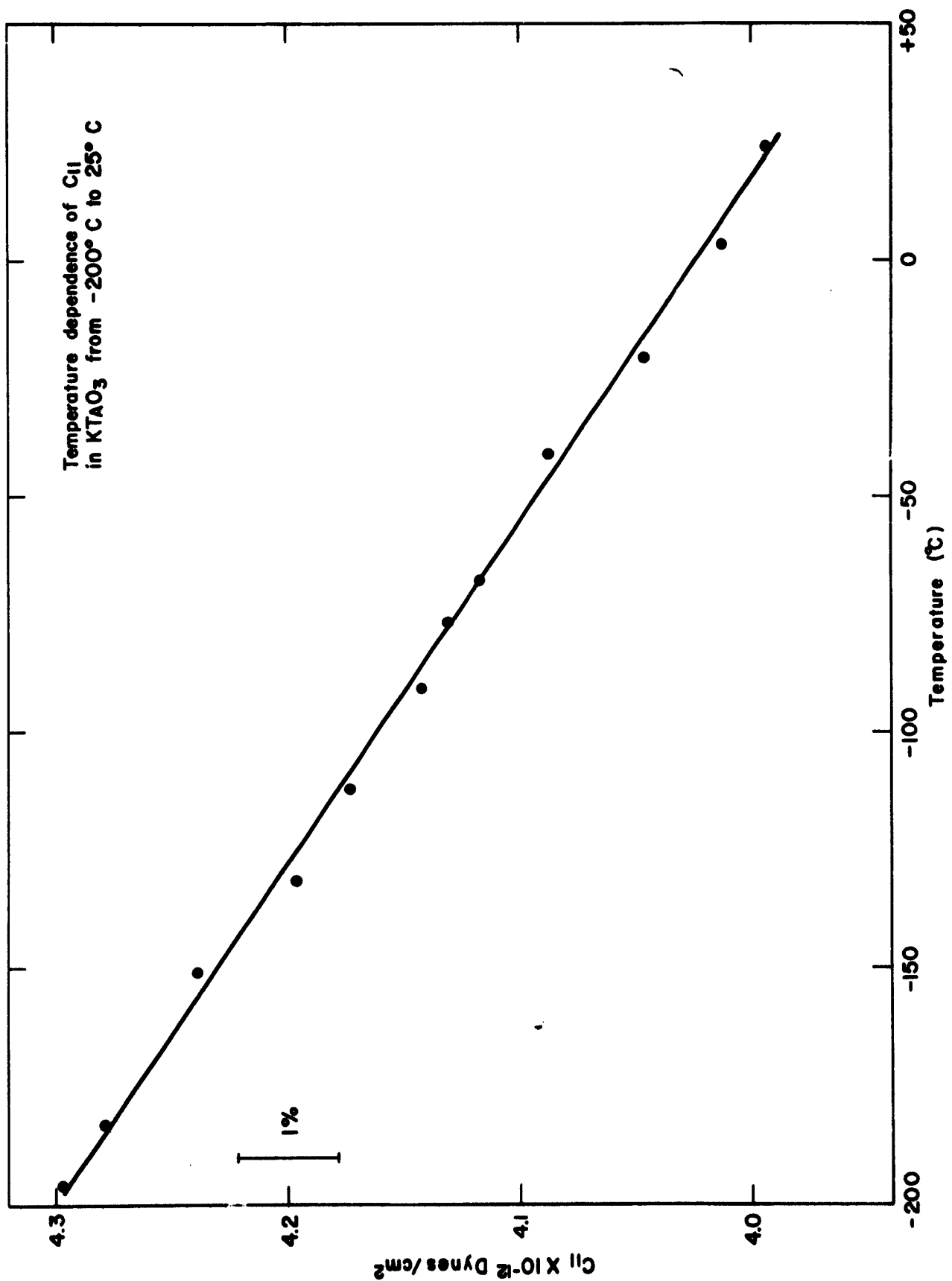


FIGURE 17



## 7. LOW TEMPERATURE DIELECTRIC CONSTANT OF SrTiO<sub>3</sub>

The dielectric constant of single crystal SrTiO<sub>3</sub> has been measured from 2°K to 60°K. These measurements were made on a small disc at a frequency of 100 Kc/sec. The results are shown in Fig. 18 and are in substantial agreement with the values reported by Weaver.<sup>1</sup> The data were fitted with an expression of the form derived by Barrett<sup>2</sup> for the low temperature dielectric constant of perovskite type crystals. The best fit was obtained with the expression

$$\epsilon = \frac{C}{T_1/2 + \coth T_1/2T - T_c}$$

with

$$C = 8.72 \times 10^4$$

$$T_c = 43^\circ\text{K}$$

$$T_1 = 110^\circ\text{K}$$

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<sup>1</sup>H. E. Weaver, J. Phys. Chem. Solids 11, 274 (1959).

<sup>2</sup>J. H. Barrett, Phys. Rev. 86, 118 (1952).

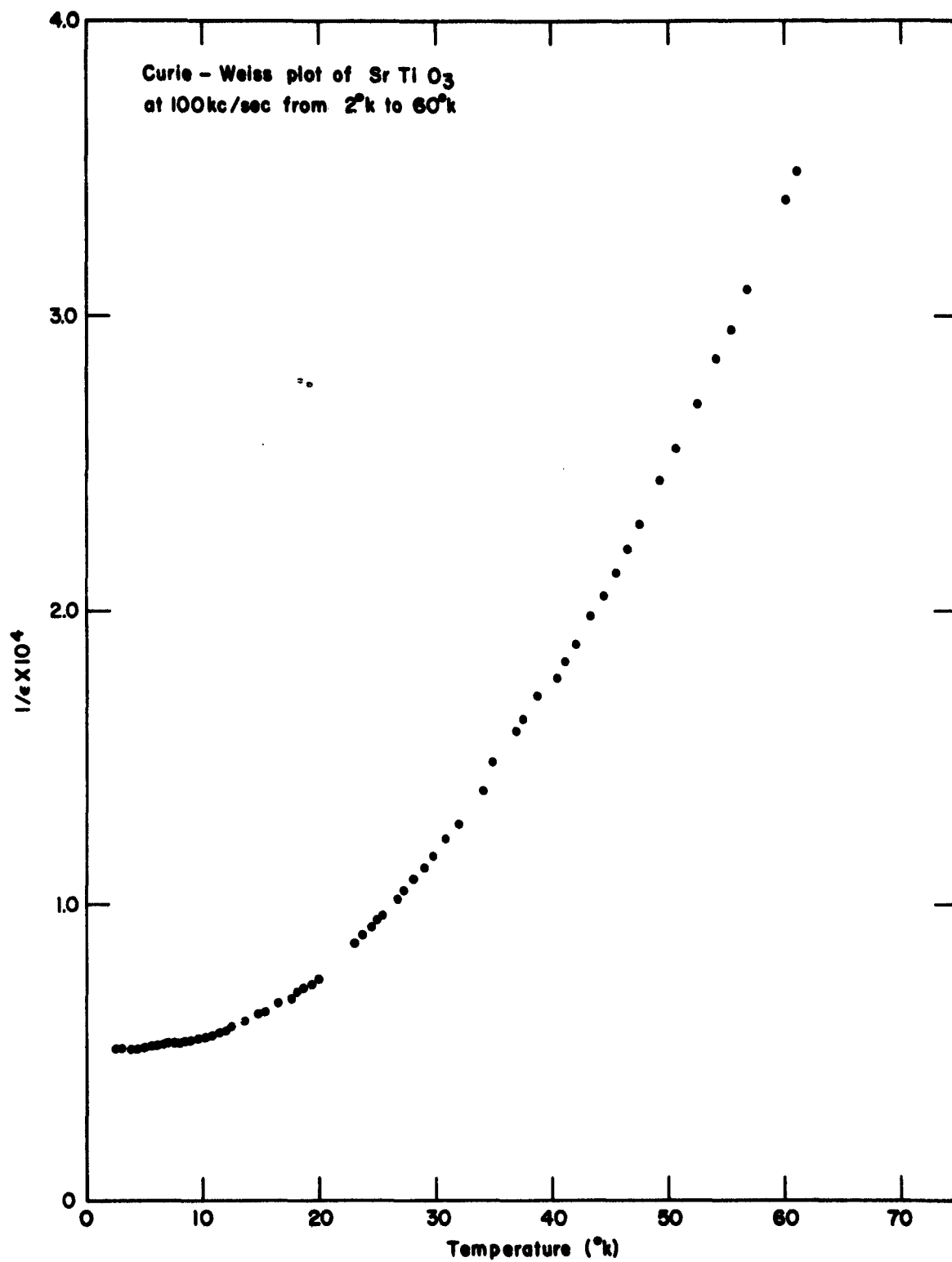


FIGURE 18

## 8. LOW TEMPERATURE DIELECTRIC MEASUREMENTS OF $\text{KTaO}_3$

The dielectric constant and loss tangent of single crystal  $\text{KTaO}_3$  were measured from 2°K to 80°K. The capacitance and equivalent parallel resistance of a parallel plate capacitor of circular cross section with a  $\text{KTaO}_3$  dielectric were measured at 100 Kc/sec in order to determine the dielectric constant and loss tangent. The results are shown in Fig. 19 and Fig. 20. The dielectric constant data are fitted with Barrett's expression

$$\epsilon = \frac{C}{T_1/2 \coth T_1/2T - T_c}$$

with

$$C = 6.025 \times 10^4 \quad T_c = 13.4^\circ\text{K} \quad T_1 = 42^\circ\text{K}$$

The agreement with K-band data at the higher temperatures is quite good.

The large peak in the loss tangent in the vicinity of  $T_c$  indicates that there may be an actual ferroelectric transition at this temperature. A comment should be made on the magnitude of the loss tangent at the higher temperatures. At 25°K the equivalent series resistance of the capacitor, its contacts and leads is of the order of one ohm or less. A large portion of this resistance is probably due to the lead and contact resistance (the lead resistance was measured to be about 0.1 ohms but the resistance of the silver electrodes on the sample has not been measured). Thus, the actual losses of the dielectric at temperatures above about 10°K are much smaller than measured here. These errors are of no consequence in the vicinity of the peak in the loss tangent since the series resistance is as large as several hundred thousand ohms and the lead and contact resistance remain essentially constant with temperature. Hence the peak should actually be even more pronounced than the one shown. For this reason no attempt was made to fit the experimental curve.

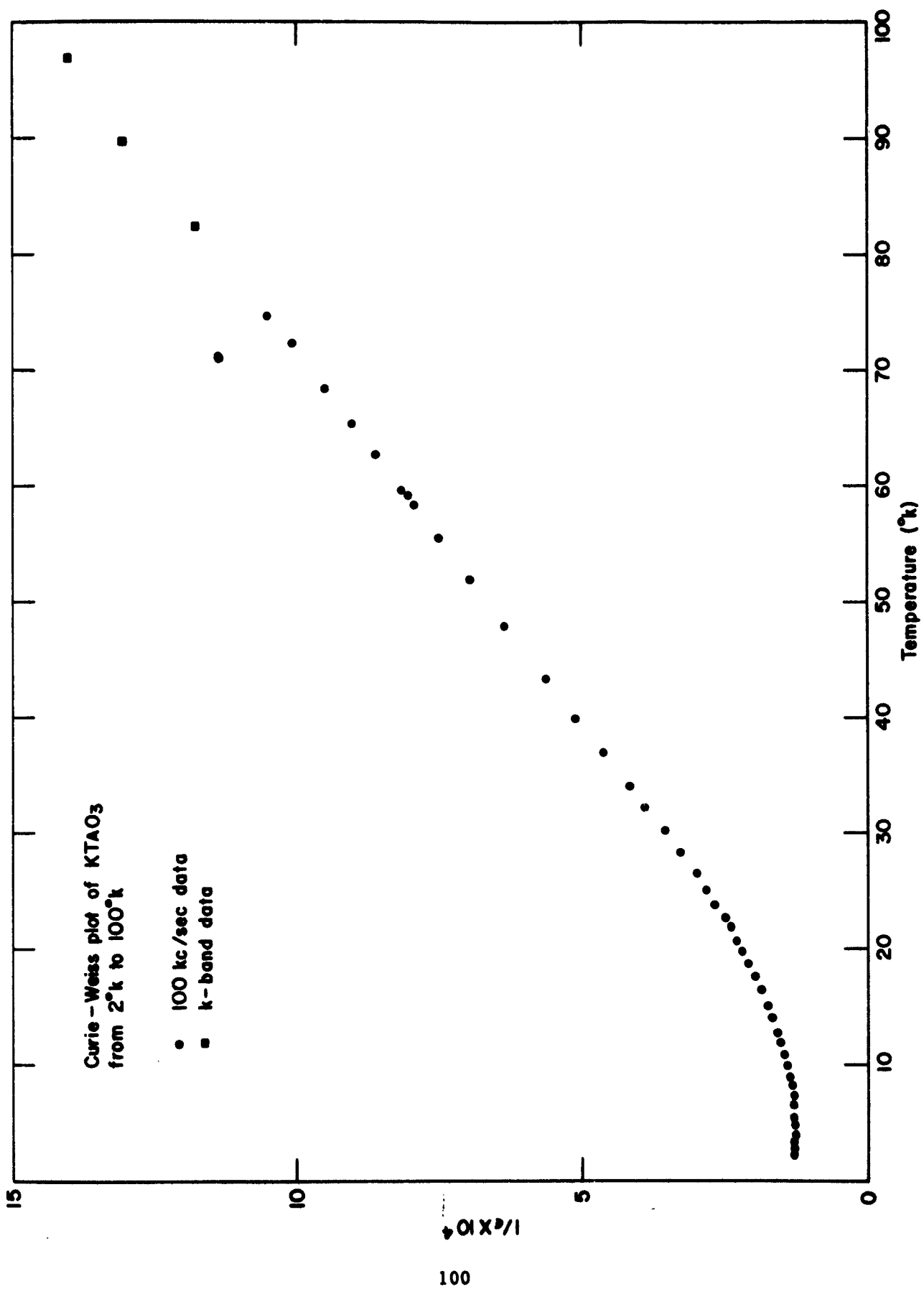


FIGURE 19

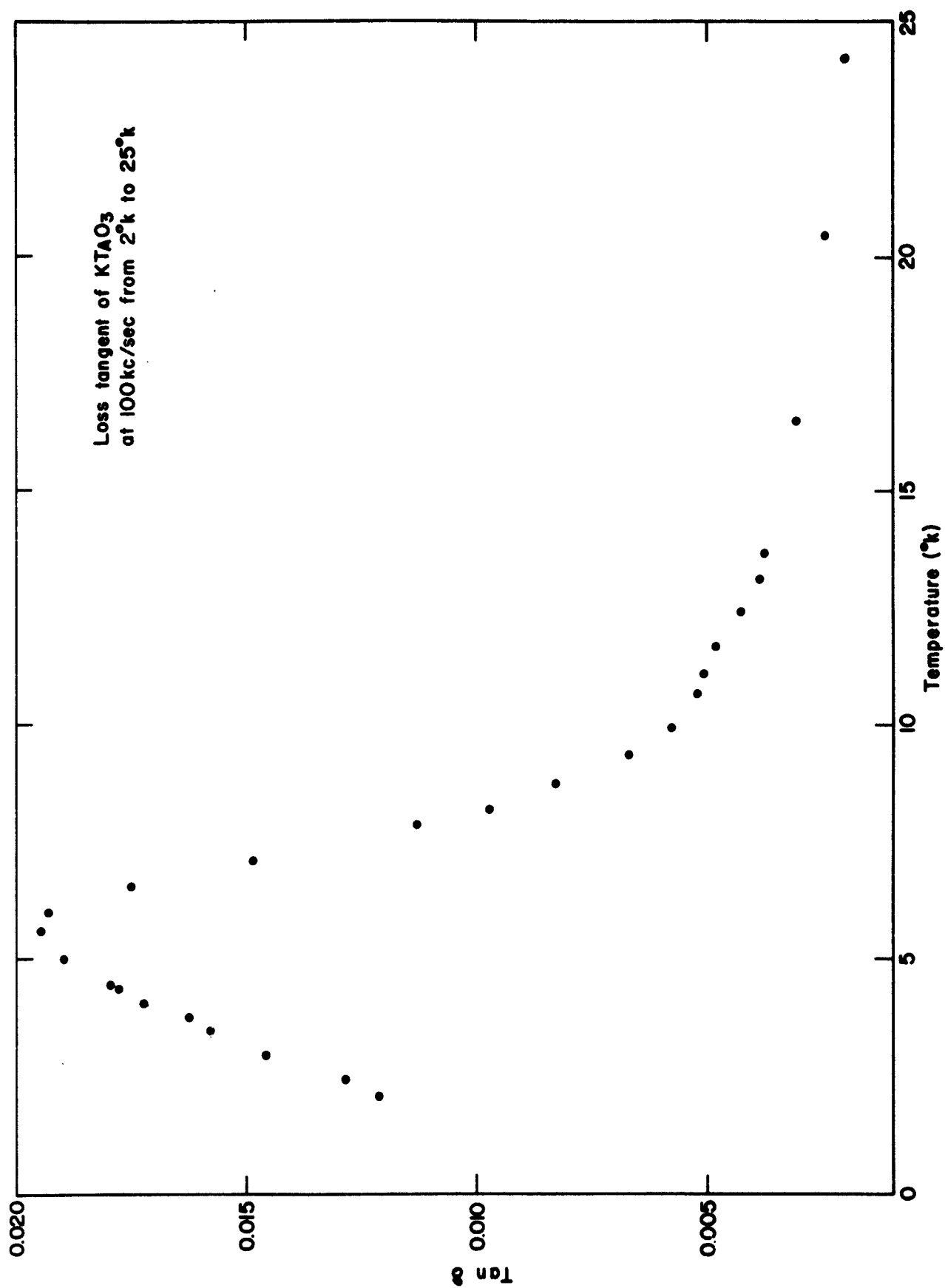


FIGURE 20

## 9. ORAL PRESENTATIONS

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| <p>UNCLASSIFIED</p> <p>1. Ferrites<br/>2. Microwave properties</p> <p>I. B. D. Silverman<br/>II. R. I. Joseph<br/>III. W. M. Winter</p> | <p>Raytheon Co., Waltham, Mass.<br/>INVESTIGATION OF THE MICROWAVE PROPERTIES OF FERROELECTRICS by B. D. Silverman, R. I. Joseph, and W. M. Winter. Final report 20 Jan. 1961 - 19 Jan. 1963. 105 pp. incl. diagr. (Report S-528). Contract AF19(604)-8005.</p> <p>Unclassified report</p> <p>A systematic and fundamental study has been made of the microwave properties of ferroelectric materials with the perovskite structure. The quantities singled out for investigation are nonlinear dielectric constant, microwave losses and electrostriction. The comparison between theory and experiment is discussed.</p> |
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